

CHARACTERISTICS OF HYDROGEN PRODUCTION VIA ISO-OCTANE
AUTOTHERMAL REFORMING FOR FUEL CELL VEHICLES

By

TIMOTHY CURTIS SIMMONS JR.

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by

Timothy Curtis Simmons Jr.

This dissertation is dedicated to my mother, Ethel Taylor.

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Timothy Curtis Simmons Jr.

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An autothermal reforming test rig was built for the purposes of studying the effects of several variables on the autothermal reforming process. In particular, this dissertation presents the manner of rig construction and results from experimentation on the effects of space velocity, air ratio and inlet temperature on the catalyst bed temperature, and the conversion and specific efficiency of the reformer using iso-octane. Specifically of interest was the separation of the effects of the inlet temperature from the definition of space velocity. The manner of rig construction and results of the experimentation are of significance for the introduction of fuel cell vehicles since the autothermal reforming of available fossil fuels is the best near term solution for hydrogen generation and little has been published on this process. As part of the study, background information was given on various hydrogen storage and production techniques and several possible fuels for reforming. The study as well outlines many difficulties and limitations of the autothermal reforming process as well as its implementation into the design of a

reformer. The experimental facility was built to include sections necessary for the storage, conditioning and reforming of the reactants as well as the conditioning and testing of the effluent.

Although the test facility was not optimized for maximum conversion or specific efficiency, several effects and interactions of the independent variables were found for the dependent variables. In particular, the interaction between inlet temperature and space velocity had a significant effect on the conversion and specific efficiency of the autothermal reformer. As a result of these findings, additional theories have been proposed as to the limiting steps in the autothermal reforming process, which are expected to aid in the reduction of autothermal reformer size and enhance the production of hydrogen for fuel cell vehicles. Finally, conclusions and recommendations for further study are drawn from the presented results.

CHAPTER I INTRODUCTION

Currently, the large-scale production of vehicles using internal combustion engines, decreased air quality and environmental degradation have heightened public sensitivity towards vehicle emissions. In order to reduce vehicle emissions, legislators have imposed emissions standards which limit vehicular emission of air quality contaminants such as carbon monoxide (CO), oxides of nitrogen (NO_x), unburned hydrocarbons (HC) and particulate matter (PM). This approach has led to the introduction of several emissions reducing devices for internal combustion engines (more efficient catalytic converters, particulate traps and the development of low sulfur fuels) and has spurred increased interest in alternative methods of mobile power production such as fuel cells.

Fuel cells are capable of producing electricity from hydrogen with water and heat as the only emissions. This aspect of fuel cell power proves to be critical because it subverts the typical generation of carbon dioxide (a greenhouse gas) for power production. Since hydrogen can be renewably produced, the life cycle of hydrogen as a fuel becomes nearly emission free.

While reduced emissions are desired for any new automotive technology, increased efficiency is also of concern. In 1996, the world's transportation sector consumed over half of the petroleum production.¹ In the United States, which consumes nearly 70% of its petroleum for transportation, tremendous strides have been taken to improve vehicular fuel efficiency through the use of lighter construction materials, advanced aerodynamics, increased electronic controls, advances in combustion and alternatives to conventional

power trains.² Vehicle implementation of alternative power train technologies such as fuel cells and gas turbines as well as energy storage devices like batteries and flywheels has been used with limited success in the marketplace due primarily to safety, range and cost issues. Of the competing technologies for alternative power trains, the fuel cell is generally perceived to have the greatest potential. This is due to its potential for high efficiency, limited emissions over a wide range of loads, low operational noise, fewer moving parts than other engines and low heat signature. There are several current challenges for competition with conventional internal combustion engines such as power density and durability as well as cost and performance issues. Although there are many challenges, research on fuel cell power has already taken several large strides towards making fuel cells commercial and it is expected that further research will help resolve the issues still remaining.

A fuel cell is an electrochemical device much like a battery. While a battery uses energy stored in its electrolyte, a fuel cell produces electricity and water from oxygen in air and hydrogen. The use of hydrogen as a fuel for transportation poses several issues. Although hydrogen has an extremely high specific energy (energy per unit weight), its energy density (energy per unit volume) is extremely low in comparison with conventional fuels such as gasoline or diesel (figures 1, 2).

This dramatically increases the fuel storage volume and severely limits space on the vehicle. Also, while hydrogen is viewed as the fuel of the future from its high specific energy and large number of applications (through thermal or electrochemical use), it lacks adequate infrastructure to support vehicle fueling.

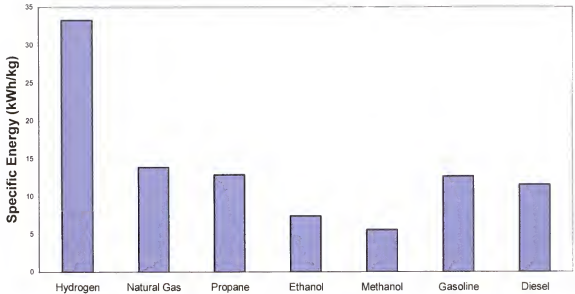


Figure 1: Specific energy of various fuels³

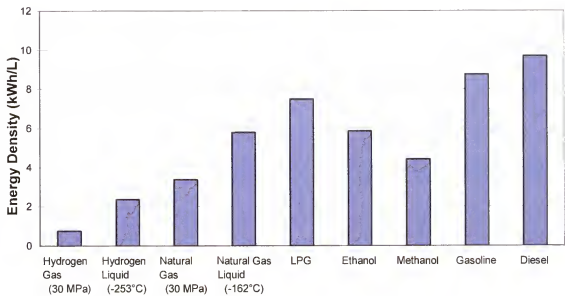


Figure 2: Energy density of various fuels^{4,5}

Since large quantities of pure hydrogen do not exist on earth, it must be produced from another hydrogen bearing substance. While there are several methods of producing hydrogen, currently nearly all hydrogen is generated from natural gas. This process of hydrocarbon fuel conversion may also be accomplished onboard a vehicle. Therefore

vehicles would benefit from the increased efficiency and decreased emissions of fuel cells while using existing fossil fuel infrastructure. Unfortunately, onboard hydrocarbon fuel processing increases fuel cell system vehicle complexity and cost, reduces efficiency and produces carbon dioxide as an additional product from the vehicle. In fact, using a hydrocarbon for hydrogen storage typically reduces the fuel cell system efficiency to that similar to many diesel electric hybrids available today, albeit typically with less regulated emissions (HC, CO, NO_x). Thus hydrogen is the best fuel for fuel cell vehicles, although proper study of methods of onboard hydrocarbon fuel processing is necessary until advances are made in methods of hydrogen storage and a transition is made to a hydrogen refueling infrastructure.

Although the method behind large fuel processors for hydrogen production from natural gas is a mature technology, an automotive scale fuel processor (potentially using other fuels) is needed to provide a hydrogen rich fuel acceptable for a fuel cell stack. In scaling down the fuel processor for vehicle applications, several critical issues arise. These include fuel cell system contamination from specie such as sulfur and chlorine which may be found in the fuel, the removal of carbon monoxide (a fuel cell contaminant) production from the processor effluent, and thermal integration of the processor. The addition of the fuel processor potentially lengthens the time necessary for start-up, shutdown and response for the fuel cell system.

Reformer Types

The University of Florida Fuel Cell Research and Training Laboratory, started in 1994, has completed several studies on the steam reforming of methanol, which is the same method used in large scale plants to produce hydrogen from natural gas. Steam reforming produces a hydrogen rich mixture through an endothermic reaction of steam

and fuel, which occurs in an externally heated catalyst bed. Unfortunately, steam reforming has serious disadvantages for transportation applications. Due to resistances in heat transfer, steam reforming does not generally respond quickly to transient loads commonly found in vehicles and typically requires long periods of time for start-up. In some cases, start-up time alone for a fuel cell vehicle using steam reforming is 45 minutes.

Partial oxidation reforming is another type of fuel processing in which the wall heat transfer limitations of a steam reformer are removed by providing heat for the reaction through a combustion of a portion of the fuel inside the chamber before the catalyst bed. Water and additional fuel are typically injected after the combustion and pass through the catalyst bed for the steam reforming process to occur. Although associated with a fast start-up time, this process unfortunately provides limited efficiency since more of the thermal energy released in the combustion is lost in the exhaust or is not effectively used in the catalyst. Also, due to the higher operation temperature, more CO is produced which increases the complexity and cost of the fuel processor for CO reduction.

Autothermal reforming combines the steam and the partial oxidation reforming methods. In this case, air, fuel and water pass through a catalyst bed where it is both combusted and reformed. The close proximity of the combustion and reforming provides better heat integration and thus increased efficiency over the partial oxidation reformer while the internal combustion provides better response than steam reformers. The temperature of operation is lower than that of a partial oxidation reformer, thus less fuel processor complexity and cost is necessary for CO cleanup. Therefore a hydrocarbon

fueled fuel processor based on autothermal reforming provides one of the most acceptable near term method of supplying hydrogen for fuel cell vehicles.

Thus it was deemed important to begin an investigation into the subject. Unfortunately, the fuel cell laboratory had neither the space nor the existing equipment to allow for the study of autothermal reformers, thus a new laboratory addition was designed and commissioned. This addition was designed as an experimental test facility including office space that doubles as a control room and laboratory space. With the additional space, a project was undertaken to design and construct a permanent experimental test rig to investigate various aspects of autothermal reforming. The rig was built in order to insure maximum safety and flexibility to encourage continued research into fuel processing. The rig provides the vaporization and mixing necessary to study many different fuels at various flow rates. The reformer itself was built in interchangeable sections to allow for a variety of configurations and thus may operate in either partial oxidation or autothermal modes (steam reforming mode is also possible with a redesign of a section). The rig also allowed for gas sampling and on-line gas detection of several species for an inspection of rig performance. Many of the critical parts of the rig were controlled by a computer program, which also provided data acquisition.

For the current investigation, the air ratio (equal to the inverse of the equivalence ratio), inlet temperature and space velocity (proportional to catalyst bed flow speed) of the autothermal reformer were chosen as independent variables to study their effects on the dependent variables: bed temperature, specific efficiency and fuel conversion. The specific efficiency was defined as the ability of the reformer to convert the fuel utilized in

the reformer into products beneficial to the fuel cell system (hydrogen, carbon monoxide and heat). Fuel conversion conveyed the ability for the reformer to utilize the fuel pumped into the reformer. The catalyst bed temperature provides additional support for the results of the specific efficiency and conversion. While the specific efficiency and conversion of the reformer were critical variables to the overall fuel cell system, the independent variables were chosen for their potential to have a great effect on the dependent variables as theoretically determined by either thermodynamics or catalysis.

Background on Fuel Cells

Sir William Grove is generally regarded as the inventor of the first fuel cell. In 1839, he was able to produce electricity by oxidizing hydrogen with oxygen through a sulfuric acid electrolyte. Due to the nature of the scientific and material challenges at the time, progress towards a working product was quite slow. Towards the end of the 19th century, the dawn of the internal combustion engine and the use of petroleum decreased interest in fuel cells until in the 20th century. Francis T. Bacon engineered the first feasible application of fuel cell power by employing a 5 kW alkaline electrolyte fuel cell for a welding machine and other devices in 1959. Fuel cells were further used for power in the NASA space program as an alternative to heavy batteries, very large solar cells and unsafe nuclear power for manned missions. NASA began using fuel cells in the Gemini and Apollo space missions and has continued their use into today's space shuttles.⁶

Fuel cells were first seriously considered for terrestrial transportation applications in 1973 with the onset of the first US oil crisis.⁶ Support for fuel cell power continues due to the concern of utilizing non-renewable resources for power and the impact of fossil fuel emissions on air quality. Spurred by these factors, many technological

breakthroughs in fuel cells for transportation have reduced the cost and size of the fuel cell and allowed for possible competition with typical vehicular powertrains.

There are five types of fuel cells that are currently being developed each named after their type of electrolyte. The fuel cells which typically operate at lower temperatures, phosphoric Acid fuel cell (PAFC), proton exchange membrane fuel cell (PEMFC) and alkaline fuel cell (AFC) (150-200°C, 80-120°C and 80°C respectively), are generally considered to have potential for power generation possibilities for vehicles. This is due to the expensive exotic materials necessary and increased time required for load transients, start-up and shut down associated with higher temperature fuel cells. Of the low temperature fuel cells, the PEMFC has grown to be the most accepted type by the automotive sector since it starts faster, is smaller, lighter and potentially cheaper than the PAFC. The PEMFC can also use air for the oxygen supply whose CO₂ concentration (>350 ppm) typically poisons an AFC.⁷ Due to the increased interest in using the PEMFC for transportation applications, it has been engineered for a high power density (typically over 1 kW per liter), high efficiency and quick adaptation to load changes compared to many other types of fuel cells. Unfortunately, due primarily to the low operating temperature, more platinum catalyst is required for the electrodes than with higher temperature fuel cells. This increases the cost of the fuel cell and makes the cell prone to poisoning by small fractions of carbon monoxide (>10 ppm) and other impurities in the fuel stream. Research is continuing into finding more CO resistant and lower cost catalyst materials, as well as reducing the amount of catalyst necessary for optimal performance.

Several concept cars have been produced in order to prove the benefits and attack the pitfalls of the technology. One such example is the Ford P-2000 produced in 1999 (figure 3). It attains 67 miles per gallon (gasoline equivalent) with a 75 kW fuel cell operating on pressurized hydrogen gas. Although there are no emissions other than water vapor and heat, it has a range of only 100 miles, which is well below the typical 250 to 400 miles for a conventional vehicle. Thus, research must continue not only to increase the range, but also to increase the system efficiency, whose total potential has yet to be fully realized.



Figure 3: Ford P2000: A hydrogen fueled proton exchange membrane fuel cell vehicle⁸

Each application of fuel cells requires additional equipment to supply hydrogen and direct the output power. As with the application of any method of power production, the additional plant reduces efficiency and increases size and weight of the system. Thus the hydrogen supply, fuel cell stack, the system components and their integration must be as efficient as possible over typical operational loading.

Hydrogen Supply

In terms of onboard hydrogen supply, the storage of pure hydrogen provides the simplest fuel cell vehicle system and the highest vehicle efficiency. Unfortunately this necessitates greater fuel storage volumes for a conventional vehicle range (figure 4) and the necessity to build a hydrogen refueling infrastructure. Assuming a shift towards a hydrogen economy for environmental reasons, several physical and chemical storage methods of hydrogen are being studied in order to reduce the fuel volume necessary for vehicles.

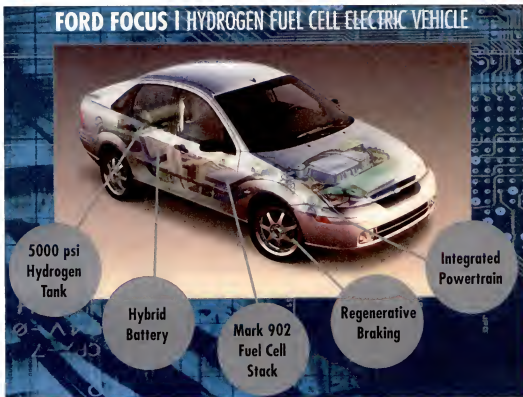


Figure 4: Ford Focus vehicle showing volume for gaseous hydrogen storage⁹

Physical Hydrogen Storage

Conventional physical hydrogen storage increases the gas density through compression, liquefaction, using physical adsorption characteristics of metal hydrides, or

carbon nanotubes. Increasing hydrogen gas density through compression exacts an energy penalty of nearly 15% to compress the gas to 34.5 MPa (5000 psi) and only provides 1/9th the energy density of gasoline at this state.¹⁰ Also compressed hydrogen is typically stored in heavy cylinders, which typically contain only 3% of hydrogen by weight in practice.¹¹ This is a significant weight disadvantage for personal transportation. Gaseous hydrogen storage does have the advantages of being relatively simple, having an indefinite storage time and the potential of very high purity. Increased storage pressure is possible but requires even heavier containment and incurs increased compression losses and safety concerns. The material used for the tanks must also resist hydrogen embrittlement, which acts in carbonaceous steel tanks to create internal voids within the container and cause possible rupture. Mass transport vehicles such as buses that have less sensitivity to increases in weight and have more available volume for fuel storage, thus gaseous hydrogen storage is a strong option for those applications.

Liquefying hydrogen raises the energy density to ¼ that of gasoline. Due to the low storage temperature (-253°C), the use of liquid hydrogen for transportation applications requires a well-insulated containment system with a boil off purge valve. Since boil-off is typically 1 to 2% per day, there is a danger of vented hydrogen collecting in combustible concentrations.¹² Also, liquefaction of hydrogen requires nearly 29% of the energy of the gas, which significantly reduces the overall efficiency of using fuel cell systems.¹³

Absorption of hydrogen to a metal hydride substrate may be an option. Metal hydrides have the potential to concentrate hydrogen to levels higher than those for hydrogen in the liquid state. When a metal hydride is heated, hydrogen atoms are

absorbed and become trapped upon cooling. The benefits of this type of storage are muted by the increased weight of the metal hydride and the bulky and complex system required for containment, charging and discharging of hydrogen. While more expensive than compressed gas, the increased weight of the metal hydride system makes this only a slightly better option than compressed gas storage in terms of hydrogen storage weight percentage.

Hydrogen containment in carbon nanotubes is another potential method of hydrogen storage. In this case, hydrogen enters an open-ended carbon tube and becomes trapped. Storage densities of 4 % by weight have been reported. While only slightly more energy dense than gaseous storage, there also have been claims of potentially increasing the hydrogen storage by 10 times that amount, thus it has been an active research area. Although many claims have been made, actual increases in hydrogen storage have yet to be realized using carbon nanotubes.⁶

While all previous fuel storage options have involved the storage of pure hydrogen, it is understood that an entire hydrogen supply infrastructure must be built in order to produce and distribute hydrogen. This requires considerable capital investment for a fuel with very little current demand in comparison to gasoline. In order to provide a transition to a hydrogen economy, hydrogen may be stored in a chemical compound for which an infrastructure already exists, in effect shifting the fuel processing from a plant to the vehicle. While local refueling station fuel reforming is possible, the current limitations on hydrogen storage as discussed above reduce its practicality for personal transportation.

Chemical Hydrogen Storage

Electrolysis, various chemical reactions and the reforming of a hydrocarbon fuel are known methods of generating hydrogen. Of these three options, electrolysis may

have the greatest potential for emission free hydrogen production. Abundant solar, wind, or other renewable energy may be used to supply the electrical power needed to separate hydrogen from oxygen in water, which then can be used for fuel cell vehicles.

Unfortunately this process must be performed on the vehicle to resolve the issue of onboard hydrogen gas storage. This limits the vehicle to solar power for hydrogen generation. Since the electrolysis of water requires more energy to generate hydrogen than can be generated by its use in a fuel cell, the use of this method of hydrogen generation gives a net energy deficit overall as compared with just using electricity from solar cells directly. Although hydrogen production from water on board vehicles is not practical, it is a possible long-range plan for renewably fueling of fuel cell vehicles once a hydrogen infrastructure is built.

Some chemical reactions have been shown to evolve large quantities of hydrogen gas. One such reaction occurs when sodium borohydride comes in contact with water and a catalyst. The catalyst turns the water and sodium borohydride to sodium metaborate and hydrogen. This process contains about seven percent hydrogen by weight, but is only slightly more energy dense (volume) than liquid hydrogen at 30% of the energy density of gasoline. Several companies have attempted to commercialize this and other methods of chemical hydrogen production with limited success. Although the volumetric energy density is higher than compressed gas, the process of regenerating sodium borohydride from sodium metaborate is quite energy intensive, thus creating a potential waste problem and/or added total life cycle emissions and reduced overall global energy efficiency.¹⁴

Processing of a conventional fuel on board the vehicle may also generate hydrogen. Fuel processing involves a thermal, or thermo-catalytic degradation of a fuel into hydrogen. One form of thermal fuel processing is known as pyrolysis, or thermal cracking. In this process, fuel is heated in the absence of oxygen (operating between about 815 – 1100°C), which thermally breaks down the fuel into its hydrogen and carbon constituents.¹⁵ This method is best suited for conversion of simple fuels such as methane as higher hydrocarbons such as gasoline and diesel may produce various residual hydrocarbons, which are not as easily cracked. The benefit of using this method with the appropriate fuel is the extremely pure hydrogen generated. Although the process produces an effluent hydrogen fraction above 90%, thermal cracking is not a viable process because of the low 8% efficiency (higher heating value of hydrogen out/higher heating value of fuel in) demonstrated in trials.¹⁵ Also, the remaining solid carbon from the process must be removed by stopping fuel flow and passing air through the reactor to burn off the carbon deposits. In practice this may become a difficult task as an integral part of a transportation fuel system due to increased carbon loading, safety and the potential for irreversible fuel cell catalyst fouling should the carbon enter the fuel stream.¹¹

In order to subvert carbon deposits and increase total hydrogen yield, fuel processing techniques which use air and water have been studied. This has resulted in the dominance of catalytic steam processing of methane as the current production method for hydrogen. Thus among the possible options for providing hydrogen from chemical storage on board the vehicle, non-pyrolytic fuel processing methods are currently considered the most likely candidate for transportation applications in the near future.

CHAPTER 2 FUEL PROCESSING

Fuel processing has been used for nearly 100 years for the production of hydrogen from natural gas for industrial applications. Through ongoing research, fuel processors have been adapted to use a variety of feedstock fuels. Thus fuels such as gasoline and diesel, which are more energy dense and easier to transport than hydrogen and which currently have a well-established infrastructure for vehicles may be chosen (figure 5).

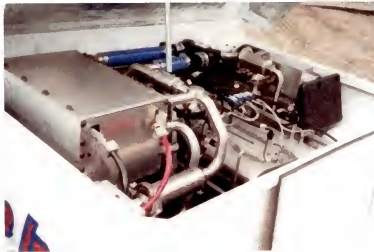


Figure 5: GM gasoline fueled fuel cell truck with fuel processor

The disassociation of a hydrocarbon fuel to reformat requires two basic steps. The first of which is the endothermic reforming step (requiring heat input) where the fuel molecule is broken into hydrogen and carbon monoxide. In order to reduce CO for PEMFCs a second reaction known as the water-gas shift reaction is employed. (equation 1)



Although the water gas shift is mildly exothermic (releasing heat), the overall reaction from fuel to low CO reformat is endothermic. Thus burning of a portion of the fuel is typically required for fuel processor operation. In addition, for use in a PEMFC, an additional CO removal process (commonly known as polishing) is also required. For fuel cell vehicles, this typically involves a preferential combustion of the CO in the reformat over a catalyst (preferential oxidation) or physical separation of the CO such as using a porous palladium membrane.¹¹ The reformer and the CO reduction steps are typically known as the fuel processor.

Due to their endothermic nature, fuel processors typically require significant time increments for start-up and transients in order to produce a required quantity and purity of hydrogen. Depending on the ability of the reformer to load-follow the hydrogen demand, additional energy buffers such as auxiliary hydrogen tanks or storage batteries may be required to fulfill electrical load requirements. Another method of satisfying loads is to over design or make the reformer larger than it needs to be for the maximum power desired. In this way, the heat necessary for transients may be supplied by the heat capacity of the catalyst bed. This option adds mass and volume to the power plant, potentially decreases the power density of the plant and thus limits its ability to compete with the internal combustion engine it may replace. In order to reduce the negative effects of fuel processing, several reforming methods have been developed to reduce the size, mass and transient time.

Reforming Methods

Currently, there are three primary methods of reforming being studied for automotive use. They include steam (SR), autothermal (ATR), and partial oxidation

(POX) reforming. Each type is distinguished by the technique of introducing heat for the reforming process.

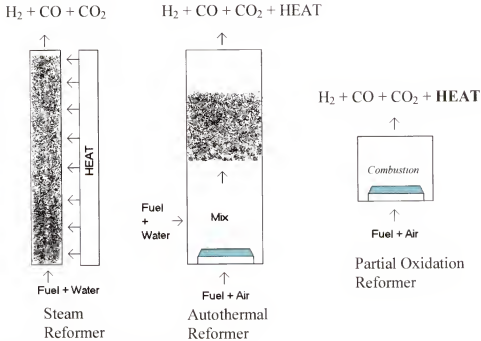


Figure 6: Various types of reformers

Important Reformer Definitions

In order to describe these reactors, several relevant variables must be defined.

The gas hourly space velocity (GHSV) gives a measure of the volume flow rate of specie through the catalyst bed.

$$GHSV = \frac{(\text{Volume flow rate per hour})}{(\text{Catalyst volume})} \quad (2)$$

The volume flow rate is typically calculated using the inlet conditions of the reactor and the catalyst volume is typically the volume of the catalyst in the bed. Unfortunately there is no current standard for inlet conditions to adequately calculate space velocity thus the temperature and pressure should also be given. In order to provide some consistency, a liquid space velocity may be provided for some applications. While the liquid space

velocity provides a measure of the mass flow rate, the temperature and pressure at the entrance are still required for the volumetric flow rate calculation. Other common variables used to characterize reformers include the air ratio (AR), and the steam to carbon ratio (S/C).

$$AR = \frac{\left(\frac{A}{F}\right)_{actual}}{\left(\frac{A}{F}\right)_{stoichiometric\ combustion}} \quad (3)$$

$$S/C = \frac{(n_{H_2O})}{(x \cdot n_{C,H,O_2})} \quad (4)$$

In equation 3, $A/F_{stoichiometric\ combustion}$ is the moles of air to the moles of fuel in a stoichiometric combustion and $(A/F)_{actual}$ is the actual molar air to fuel ratio used. In equation 4, n_{H_2O} and n_{C,H,O_2} are the number of moles of water and fuel respectively and x denotes the carbon number for the fuel. An additional concern is that of reformer efficiency (η_R). While defined differently in various texts, the basic definition will be used here.

$$\eta_R = \frac{(n_{H_2} \cdot LHV_{H_2} + n_{CO} \cdot LHV_{CO})}{(LHV_{fuel\ in})} \quad (5)$$

CO is included in the definition of the reformer efficiency since it is typically either used in the fuel cell directly, burned to increase fuel cell plant efficiency or converted to additional hydrogen through the water gas shift reaction. Additionally, a reformer may be described in terms of conversion (C_f). This is a ratio of the unconverted or fuel remaining in the effluent of the fuel processor, to the fuel input to the processor.

$$C_f = (1 - fuel_{unconverted} / fuel_{in}) \cdot 100 \quad (6)$$

Conversion is an extremely important factor since any unconverted fuel is potentially detrimental to some of the other fuel cell system components as well as representing a direct efficiency loss to the power plant.

Steam Reforming

Hydrogen production for stationary industrial applications such as ammonia, have used the method of steam reforming (SR) of natural gas for more than a century. This well known reforming process injects a mixture of vaporized water and fuel over an externally heated tube filled with catalyst to generate hydrogen, CO and CO₂. The catalyst helps in lowering the temperature necessary for the reforming process to occur and assists in the water gas shift reaction. The lower reaction temperature also provides a more complete water gas shift reaction, which lowers the CO substantially (typically to 0.5 - 1% in reformat). Although steam reforming is the most thermally efficient and provides the most desirable H₂/CO concentration ratio in the reformat as compared with the other methods of reforming, it lacks the dynamic response necessary for the rapid transient loads experienced by vehicles. This is primarily due to heat transfer limitations manifested in the size of its catalyst bed and the dependence on conduction to supply external heat to the catalyst for reforming. Although the issues of transient response, start-up time, size and weight still remain a problem, several fuel cell systems for transportation applications have been created which employ this type of reforming technology using methanol as a fuel.¹⁶

Partial Oxidation Reforming

In order to efficiently handle the rapid start-up and transients required by transportation applications and reduce reformer size, other methods of heat delivery to the reactor may be employed. Partial oxidation (POX) reformers deliver heat within the

reformer and can quickly generate hydrogen using a fuel rich combustion, which provides very short (in comparison to SR) start-up times. In this combustion, the fuel is burned with air at less than stoichiometry to supply heat for the endothermic reforming reaction of the fuel not consumed in the combustion. The high local temperature of the combustion in a POX (typically 1200 to 1500°C) thermally disassociates the fuel into a mixture of several products including hydrogen, which eliminates the need of a catalyst bed. Without a catalyst bed, the reformer can process heavier and potentially contaminated fuel distillates much more quickly than catalytic processes. While possible fuel impurities may not damage a POX reformer, several may foul or deactivate catalysts in the fuel cell, thus they must be removed before the reformat can be passed to the stack to produce electrical power. POX reforming has been used in large-scale industries, although it is not as well known as steam reforming for transportation applications since control of the reaction in scaled down versions is quite difficult.¹¹ Also, the high temperatures typically evolved in a POX reformer limit the effectiveness of the water-gas-shift reaction, thus promoting a high concentration of CO in reformat (10–30%).

Catalytic Partial Oxidation Reforming

In order to lower the temperature of the reaction and thereby decrease the CO fraction, a catalyst may be used to support the combustion reaction. This process, known as catalytic partial oxidation (CPOX), typically uses a supported platinum-metal or nickel based catalyst, which lowers the reaction temperature to between 800 and 1000°C.¹⁷ Catalyzed or un-catalyzed POX reformers tend to produce less hydrogen per fuel molecule than does steam reforming since a portion of the fuel stream is used for heat. The high temperature necessary for disassociation of the fuel molecule in the reformer also increases the cooling load between reactors. Thus utilization of the thermal energy

contained in the effluent of the reformer is essential for optimum efficiency. This becomes very difficult in practice and leads to lower overall efficiencies than SR. Also, since air is used in combustion, nitrogen remains in the reformat, which lowers the overall hydrogen concentration in the fuel cell stack. This potentially lowers the overall fuel cell plant efficiency by requiring a higher reformat flow rate through the anode and thus promoting a lower utilization of the hydrogen in the stream.¹⁸

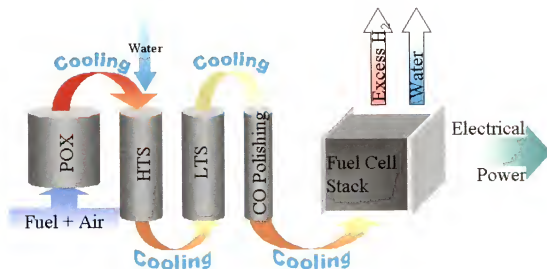


Figure 7: Partial Oxidation Reforming Subsystem

POX and CPOX reformers do not require steam for operation, which decreases reformer complexity. Although the reformer does not require steam, water is still typically needed to reduce the CO concentration in the reformat for low temperature fuel cells, thus POX and CPOX reformers for on-board hydrogen production are rarely shown without water injection and water gas shift clean up steps (figure 7). This step typically manifest itself as high (HTS around 400°C) and low temperature shift (LTS around 200°C) catalyst beds.¹¹ The temperatures given are approximate averages since the actual temperatures of the beds vary due to the exothermic water gas shift reaction occurring

within the beds. The beds contain different catalysts, which are designed to operate in their respective temperature ranges, thus heat exchangers are placed between beds to ensure lower temperatures and greater CO conversion in each subsequent bed. The additions of the high and low temperature shift converters increase system complexity, size and cost, but are necessary when using POX reactors to obtain acceptable reformat for application in PEMFCs.

In order to reduce heat losses in the reformat (thus increasing efficiency), reduce the fuel processor complexity and take advantage of the high temperature reaction kinetics of the POX, autothermal reformers (ATR) are being produced. Autothermal reformers are designed to combine both partial oxidation and steam reforming technologies. The ATR uses a small (in comparison to a steam reformer) reforming catalyst bed with internal combustion for heat integration. In effect, an ATR is similar to placing a high temperature shift bed and the water necessary for the conversion into a CPOX reformer. The operational temperature, while substantially lower than a POX reactor is generally higher than that for a steam reformer, thus promoting faster reaction rates while allowing a smaller size of the catalyst bed. The internal combustion provides the energy input necessary for fast transients while the catalyst allows for a lower reaction temperature for a more desirable hydrogen to CO ratio in the reformat than POX and a higher overall efficiency.

Although the operational temperature is lower than that of a POX, typically a low temperature shift converter is still required to produce reformat with sufficiently low CO concentration for low temperature fuel cells. From a systems perspective, the ATR concept suffers from the inability to use the excess hydrogen in fuel cell exhaust (tail gas)

as a source of heat energy to help the reforming process (as in a steam reformer). In order to maintain high efficiency in a fuel cell system using an ATR, the excess tail gas hydrogen is either burned for steam generation or used as heat energy to help pressurize the fuel cell stack for increased power output through utilization of a turbo expander (similar to a turbocharger). Unfortunately, the excess fuel energy from the fuel cell anode exhaust cannot be fully integrated into the hydrogen generating system and thus both POX and ATR methods incur an efficiency penalty.¹⁸ The efficiency penalty for POX is typically greater than that for ATR due to the increased air (and thus N_2) necessary for the burn and the additional cooling necessary for the higher temperature POX reactor between lower temperature water-gas shift beds. Due to the actual implementation of heat integration, catalyst type, feed fuel type and definition of efficiency, the actual efficiencies of ATR and POX reformers may vary significantly.^{19,20} Although autothermal reformers are still in the experimental phase, they may offer the best combined characteristics of any the reforming option for automotive applications.¹⁸

Potential Fuels for Autothermal Based Fuel Processing

Even though an autothermal reformer-based fuel processing system is the most likely method to supply hydrogen with the transient response, range and limited capital investment for fuel infrastructure necessary for personal transportation applications, an appropriate feedstock fuel must be chosen for the storage of hydrogen. There are several factors, which must be considered such as the energy density, ease of reforming, supply infrastructure, cost, and safety.

There are several mass produced fuels, which may be used for hydrogen storage. These fuels currently include diesel, gasoline, methanol, ethanol, natural gas and propane. Since containment volume and handling are issues, figure 2 would indicate that high

energy density liquid fuels such as gasoline, diesel or propane should be used. This does not take into account other reforming factors such as possible hydrogen production from a fuel as well as the amount of water necessary to reduce CO in the effluent.

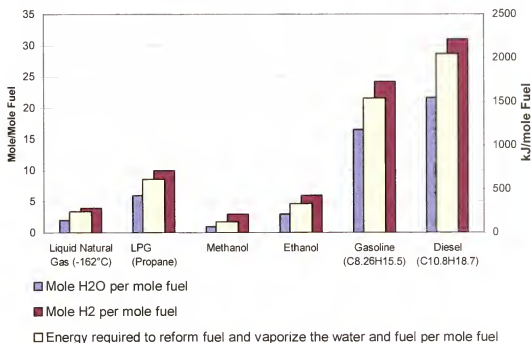


Figure 8: Comparison of water necessary, energy necessary and hydrogen output to reform different liquid fuels³

Thus figure 8 was calculated based on an overall reforming reaction using the fuel and water as the reactants and hydrogen and carbon dioxide as products. It shows that while gasoline, diesel or propane produce more hydrogen per mole of fuel than do methanol, ethanol or natural gas, much less water and energy is needed in order to complete the reforming reaction per mole of fuel. Since both the water and the fuel necessary for hydrogen production must be carried on the vehicle, a comparison of total volumes and masses per mole of hydrogen is necessary.

This can be calculated by adding the energy necessary for fuel reforming to carbon dioxide and hydrogen with the energy required for vaporization of both the fuel and water

and dividing by the number of hydrogen atoms produced in the reaction. The energy for vaporization can then be converted into an equivalent volume of the fuel and added to the volume the total water and fuel necessary to produce a mole of hydrogen. Then the densities of both the fuel and water can be used to find the total mass per mole of hydrogen produced.

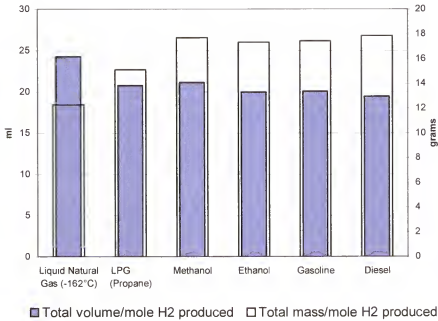


Figure 9: Comparison of total fuel and water volumes and masses necessary to produce 1 mole of hydrogen for candidate liquid fuel hydrogen carriers

Figure 9 shows that all fuels considered have very similar volumes and masses per unit hydrogen output. Thus, the fuels do not show the reduction in mass or volume of onboard stored reactants as was indicated by their respective energy densities. This is due to the amount of water (which is assumed to be stored onboard) necessary for reforming. If one examines the fraction of water to fuel required for hydrogen production, the influence of energy density becomes more evident.

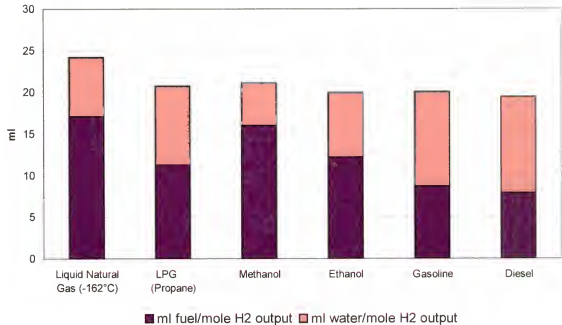


Figure 10: Comparison of fuel and water fractions per mole of hydrogen

Figure 10 indicates the significant effect of water on the total volume necessary for fueling fuel cell vehicles. It is important to note that since water required for reforming must be both deionized and rigorously filtered to remove any catalyst deactivating constituents, the actual cost may be more than conventional drinking water. In terms of reducing the volume of fuel required for a given power output, diesel fuel is the best of the fuels examined although many fuels are similar. It also must be noted that since water is produced in the fuel cell that it may not be necessary to carry onboard all of the water needed for the reformer.

Although diesel fuel has the greatest hydrogen storage potential of the fuels chosen for hydrogen production, it is one of the most difficult fuels to reform. This is due to the high concentration of sulfur (a fuel cell and reformer catalyst poison) found in common diesel, the high thermal energy necessary to reform the fuel and the high potential for carbon evolution during the reforming process. Although gasoline has been also known

to form carbon from combustion and contain sulfur, it is important to note that the range of optimal (for reforming) reactant ratios with diesel is smaller than for gasoline and that gasoline typically contains less sulfur than diesel. Thus gasoline is easier to use for applications involving transients and requires less desulphurization. Therefore the reforming of diesel fuel has received less attention than for other fuels.²¹ Most diesel reforming activity has centered on large scale POX reforming for stationary applications such that sulfur can be economically reduced through the plant, the process can operate at near steady state and the effluent thermal energy can be efficiently utilized. Although reforming of all of the fuels mentioned has been attempted using autothermal reforming, methanol and gasoline have received the most attention.

Methanol Fueling

Methanol has been considered for use in fuel cell systems due to its ease of reforming (low reformer temperature) and its high hydrogen to carbon molecular ratio. Methanol is currently produced from natural gas although it may be produced from cellulose for a carbon neutral system. If methanol consumption grows to encompass fuel cell vehicle applications, large quantities of currently stranded off-shore natural gas may be utilized. Also, some natural gas energy resources are currently flared because it lacks the market base to sequester it. Unfortunately, methanol contains only half the energy density of gasoline, and like ethanol, has little existing infrastructure for transportation applications. The use of existing gasoline and diesel infrastructure is possible although methanol cannot simply be placed in existing diesel rated hoses or tanks due to material incompatibilities. Thus, there would be an additional cost to retrofit existing fuel lines or purchase new fueling stations for methanol service. Although expensive (in 1998, \$300,000 for garage and \$400,000 for filling station for 200 methanol fueled buses), the

refueling station costs are much less than for propane, hydrogen or natural gas.^{22,23} Thus from a market standpoint, methanol is more expensive than conventional fuels to implement for vehicle applications.

There are also several safety considerations with the use of methanol. Methanol produces a nearly colorless flame that makes it difficult to detect flame propagation and methanol is also toxic if ingested or comes in skin contact for an extended period of time. This also increases the cost of implementing the fuel. Thus if one expects a fuel cell powered vehicle with similar fuel prices, convenience and range as they currently receive from internal combustion engine cars, a petroleum-based fuel similar to gasoline or diesel must be considered.

Gasoline Fueling

Gasoline is a well-established, low unit energy cost fuel. Due to the contaminant requirements of fuel cells, the gasoline pumped into vehicles today would not be the same as that which would be used for fuel cell vehicles. Current vehicles require additives to enhance the combustion and corrosion characteristics of gasoline. These additives can degrade fuel cell system performance and are not necessary for the reforming process.

Sulfur is an additional gasoline constituent (30-300 ppm in industrialized countries), which must be removed (to below 0.1 ppm) to limit its poisoning effect on both the fuel cell and reformer catalysts.^{24,11} Since sulfur also poses a possible environmental threat when burned in internal combustion engines though increased acid rain contributors, there is already considerable interest in reducing sulfur in conventional gasoline. Until sulfur is removed from gasoline, it may be removed on the vehicle using a process known as HydroDesulfurization (HDS) in which sulfur compounds are

converted to H_2S over a nickel or cobalt-molybdenum oxide catalyst. H_2S is subsequently absorbed in a zinc-oxide bed to form zinc sulfide. Both beds operate between 350°C and 400°C and thus can be placed in the same vessel.



The zinc-oxide bed must then be replaced which leads to additional operation hazards should the bed become ineffective.¹¹ While H_2S would most likely adsorb to the catalyst in a fuel cell before exhaust should the zinc-oxide bed not be replaced, H_2S is an extremely toxic compound in levels above 100 ppm. Designing a bed replacement scheme may increase fuel cell system complexity and cost, but is necessary if conventional gasoline containing sulfur is used.

Another concern is the cocktail type composition of gasoline. The varying formulation of gasoline may increase the variability experienced in the reforming process. Research into the reforming potential of various gasoline constituents is ongoing, although all typical constituents may be reformed using an autothermal reformer.^{25,26} Solutions to the issue of fuel variation may be obtained with proper adjustments made to the refining process and to the operation of the reformer.²⁵

When one considers the cost for introduction, safety and the volume of storage for a range similar to current vehicles, gasoline is a very likely candidate for fueling fuel cell vehicles through a transition to a hydrogen economy.

Background theory of Autothermal Reforming using Gasoline

For gasoline fueled autothermal reformer testing, isooctane (C_8H_{18}) is typically substituted for gasoline. This substitution is made for fuel consistency because of the variable composition of gasoline and to provide theoretical basis for the results for the experimentation since not all gasoline compounds are known. Isooctane (defined with

octane number 100) is also used as a test fuel for internal combustion engines since it is typically the largest fraction specie found in conventional gasoline.

Theoretical explorations of autothermal reformer behavior in general have begun with chemical equilibrium calculations to calculate possible fractions of various products of the reaction. These calculations help to indicate optimum design set points of the reactants. Although helpful, they require knowledge of the temperature of the reactants, the possible reaction products and pressure, which are only available by experiment. Typically a constant pressure, adiabatic process with products CO, CO₂, H₂O, H₂, N₂, and C₈H₁₈ is assumed. NO_x may also be assumed in the products although it yields very small fractions due to the reaction temperature. Solid carbon as well may be assumed in the products although solid carbon formation is extremely catalyst dependent since most catalysts used for reforming are designed to inhibit coke formation. Since catalyst formulation, and the experimental autothermal reforming environment are critical factors to the products of the reaction, it is important to note that specie fractions calculated from thermodynamic equilibrium serve as a model to understand the characteristics of the reaction.

Equilibrium Calculation

Thus the program “ThermoChemical Calculator” provided by Caltech was used to perform chemical equilibrium calculations using a constant pressure adiabatic process for various S/C and air ratios assuming CO, CO₂, H₂O, H₂, N₂, and C₈H₁₈ as the products. Further, a reactant inlet temperature of 500K (similar to the vaporization temperature of isooctane) and a pressure of 1 atmosphere were used (figures 11, 12).

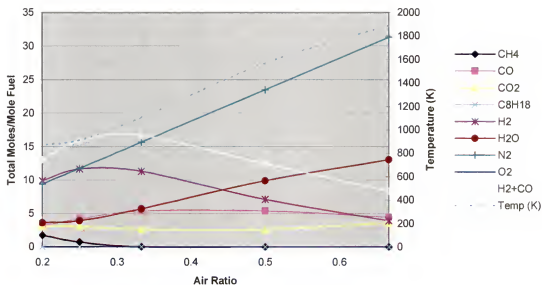


Figure 11: Molar Equilibrium Products at S/C ratio of 1

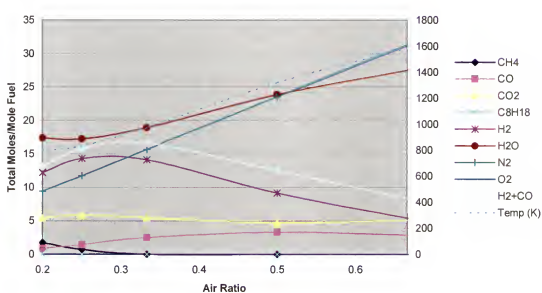


Figure 12: Molar Equilibrium Products at S/C ratio of 3

In figures 11 and 12 and as has been shown in literature with other fuels, the mole fraction of CO decreases as the S/C ratio increases. It has also been noted that the level of CO decreases with lower reaction temperature and that methane is a potential product at low reaction temperature.^{27,28,29} While CO decreases with decreasing temperature, this

is only true below around 1200 Kelvin for the constraints imposed. Above this temperature, CO actually increases with decreasing temperature. The hydrogen concentration, which peaks at an air ratio of approximately 0.3, increases with an increase in S/C ratio from 1 to 3. It is also important to note that the effect of the air ratio is much more significant to the output mole fractions of hydrogen and carbon monoxide than is the S/C ratio.

While the total hydrogen and CO product seem to be independent of S/C ratio in the graphs shown, this is not the case. If one adjusts the air ratio at a given S/C ratio for the optimum value for $H_2 + CO$ (thus the highest efficiency η), the efficiency values for a 500K inlet temperature vary by 1% between S/C ratios of 1 and 3 (figures 11, 12). Additionally, the air ratios corresponding to these efficiency values are identical. Therefore, as the S/C ratio increases, the temperature of the reaction decreases, which tends to increase hydrogen-consuming methane in the products thus lowering efficiency. This effect is more significant with the lower inlet temperature since methane is in higher concentration at lower temperatures.

The inlet temperature of the reaction may also be varied for its effect on the reaction products. An inlet temperature range of between 400 and 700K was chosen from literature based on maximum theoretically achievable values from literature for an autothermal reformer in a PEM fuel cell system.^{27,30} These inlet temperatures also correspond to values found in current operational autothermal reformers.²⁸

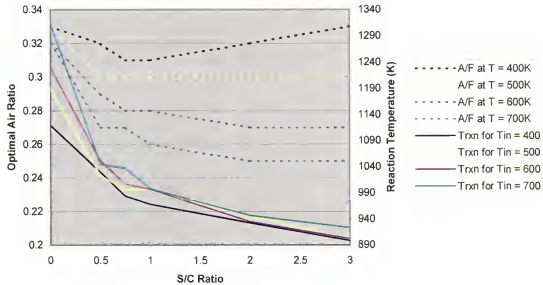


Figure 13: Optimal air ratio and reaction temperature vs. the S/C ratio

Thus by using figures 11 and 12, optimum air and S/C ratios for the maximum $H_2 + CO$ output can be found for various inlet temperatures (figure 13). It can be calculated that an increase of 300K from 400 to 700K to the inlet temperature may yield efficiency gains of 7.5% (figure 14). Also, while changing the S/C ratio from 1 to 3 changes the optimum efficiency very little at an inlet temperature of 500K, the effect of methane production is evident from the efficiency at 400K. It is also important to note that the maximum efficiency for an inlet temperature of 700K occurs at a much higher S/C ratio, and thus the fraction of CO at the maximum efficiency point is lower (4.7% absolute) than at inlet temperatures of 600K (7% absolute), 500K (13% absolute) or at 400K (nearly 14% absolute). The hydrogen product specie fraction (H_2 /all other products) varied between 30.3 and 31.8% for all inlet temperatures.

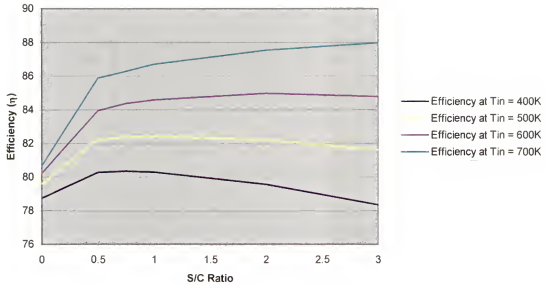
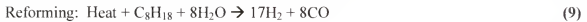


Figure 14: Reformer efficiency η vs. the S/C ratio

In order to explain the equilibrium results more fully, it can be assumed that the overall equilibrium reaction takes place in three basic steps; combustion, reforming and water-gas-shift. (equations 8-10) As a model, the fuel can be assumed to combust with the reactant air concentration at stoichiometry for heat while the remainder of the fuel and water converts to H_2 and CO . While the water-gas-shift shifts the CO generated by the reforming reaction to hydrogen, it does not add to the efficiency. Thus solely the products of the reforming reaction drive increases in the efficiency.



The most dramatic increase in efficiency occurs between 0 and 0.5 S/C ratio (figure 14). The increase grows with rising inlet temperature. With a S/C ratio of 0, the water and heat necessary for the reforming reaction comes from the combustion of the fuel with

air. Since the reforming reaction requires less energy per mole of fuel than what is released by the combustion of the fuel, the efficiency is more limited by water than by energy for a given inlet temperature. Thus the reaction is more sensitive to the S/C ratio than air ratio. When the inlet temperature is increased, the temperature of the reaction is increased, which promotes a more effective use of the water produced by the combustion for the reforming reaction. This allows for increased efficiency and a lower optimum air ratio. When water is present in the reactants, more fuel may be reformed. The water addition removes some of the burden of water generation from the combustion, and thus allows a lower air ratio for higher S/C ratios. The combination of the increase in endothermic reforming and decrease in air ratio dramatically lowers reaction temperature in this 0 to 0.5 S/C ratio range.

In the region between S/C ratios of 0.5 and 1, the trend of the maximum efficiency of the reaction changes (figure 14). This is where the regions of operation change from being water limited to energy limited process. As water is increased, its utilization for the reforming reaction decreases, thus energy is wasted in order to bring the water not used in the reforming reaction to the reaction temperature. As the inlet temperature increases, this optimum efficiency point occurs at higher S/C ratios, which again is indicative of the energy limitation. Therefore there exists a condition for the maximum efficiency for a given inlet temperature.

Water concentration in the reformate is important to the system integration of the reformer into the fuel cell power plant because it can be recycled. A solid polymer fuel cell requires water in the entering fuel and oxidant streams to help the electrolyte remain moist and conductive. Although water is necessary for PEMFC operation, the amount of

water necessary is very dependent on the manufacturer, thus further reformat conditioning may be required to adapt reformat moisture content to the needs of the fuel cell stack.

The water is also important to system integration due to the energy required to vaporize the feed to the fuel processor. The efficiency conventionally assumes that the heat for vaporization and superheating of all reactant streams also comes from the inlet fuel. This level of thermal integration may actually be somewhat difficult to achieve based on the design and operation of the rest of the fuel cell power plant. Since every fuel processor will inevitably have various methods and efficiencies for thermal integration, another measure of efficiency may be offered which assumes very little thermal integration for vaporization and thus is not dependent on plant integration. Thus another efficiency is defined to account for the energy necessary to vaporize the reactants.

$$\eta_{ES} = (n_{H_2} \cdot LHV_{H_2} + n_{CO} \cdot LHV_{CO}) / (LHV_{fuel\ in} + \Delta H_{Reactants\ to\ inlet\ temperature}) \quad (11)$$

In actual operation, the $\Delta H_{reactants\ to\ inlet\ temperature}$ could be substituted by LHV of the additional fuel required to bring reactants to the inlet temperature for an actual efficiency, which includes losses due to the method of vaporization.

Thus, although operation at higher S/C ratios will generally increase the reformer specific efficiency (η), the water vaporization load on the fuel cell system and may lower overall efficiency (η_{ES}) as in figure 15. The efficiency of an actual system in equilibrium should lie between the values displayed in figures 14 and 15 since heat energy from either the reformat or the anode flue gas can be used to vaporize the reactant feed streams and increase the total reformer efficiency. Reformer efficiency cannot be

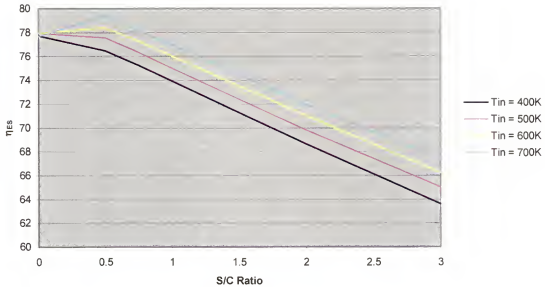


Figure 15: Reformer efficiency factor R_{ES} vs. S/C ratio

increased past that of figure 14 at the given inlet conditions since there cannot be more enthalpy in the products of the reaction than in the reactants for an autothermal reformer. In some cases the efficiency may lie below the η_{ES} due to inefficient heat transfer and not using exhaust heat from other areas of the fuel cell engine.

Although solid carbon was not included in this analysis, it is important to note that solid carbon, according to equilibrium calculations by Wieland, begins to form at air ratios just less than at the optimum CO and hydrogen production point.²⁸ Also, according to Docter, increased S/C ratio limits the onset of coke formation to lower air ratios.²⁷ Thus even though catalysts are designed to inhibit soot formation, most autothermal reformers should not operate near this regime.

There are many factors that may allow an autothermal reformer to stray from its expected equilibrium product specie distribution. The product specie was calculated assuming constant pressure and adiabatic conditions. Although a good approximation, neither of these variables are constant in an actual system due to physical constraints.

Also, the process may occur without reaching an equilibrium state. In this case, the kinetics of the reaction become important.

Chemical Reactor Basics

In order to provide some characterization of possible kinetic limitations in the reforming process, and provide a framework for the future production of reactor models, a greatly simplified analysis of the processes within a fixed bed reformer was completed. In this case, reformer can be modeled as a fixed bed flow reactor, which assumes that there is no forced mixing within the reactor vessel and thus continuous specie concentrations exist and are a function of the length of the reactor (also known as plug flow). Using these assumptions, material, energy and momentum balances are used to provide the necessary equations to describe the model.

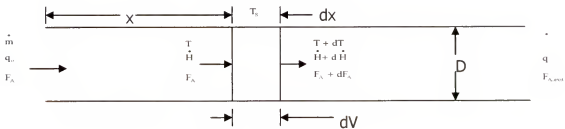


Figure 16: Model of flow through a catalyst bed

As reactants flow through the catalyst bed they are transformed into products through a net endothermic reaction (figure 16). Thus the concentration of a specie is a function of the catalyst bed depth (x) where bed depth is measured from the entrance of the bed. Since there is heat required for the reaction to occur, the enthalpy as well as the temperature in the reactor changes as well with bed depth.

Thus a material balance can be found to describe the change in specie concentration with bed depth on the section dV . Thus for steady state operation,

$$F_A - (F_A + dF_A) + r_A dV = 0 \rightarrow r_A = dF_A / dV \quad (12)$$

where F_A is the flow rate (moles/s) of reactant A, r_A is the reaction rate of the chemical equation with respect to chemical A (mol/l-s) and dV is the differential volume of the reaction zone ($dV = \frac{1}{4}\pi D^2 dx$ for cylindrical reactors). This equation can be rewritten in terms of the concentration of specie A (C_A) as

$$r_A = d(C_A q) / dV \quad (13)$$

where q is the volumetric flow rate (l/s) and C_A is in mol/l. Thus it is possible to find the bulk reaction rate for reactant A by the difference in entrance and exit concentrations if the density and thus the volumetric flow rate is constant. In this case, it is also possible to define the space velocity (τ) commonly used in fuel processor research as

$$\tau(GHSV) = 3600 \cdot V / q_o \quad (14)$$

where q_o is the inlet volumetric flow rate. Space velocity is an industry standard variable for a measure of the residence time of the reactants through the reactor. The assumption of constant density unfortunately is not the case for most autothermal reformers since molar fractions as well as the temperature vary through the reactor. Thus space velocity should be defined as

$$\tau(GHSV) = 3600 \cdot \int dV / q \quad (15)$$

In this case, the volume flow rate can be defined as

$$q = F_t RT / P \quad (16)$$

where F_t is the total molar flow rate of all specie in dV and R is the gas constant.

The space velocity can be rewritten using equation 12 as

$$\tau(GHSV) = 3600 \cdot \int dF_A / r_A q \quad (17)$$

in order emphasize the importance of both the reaction rate and the local molar flow rate to the calculation of the space velocity.

Since reactions are occurring which change the specie fractions through the reactor, the reaction rate or concentration change per unit time, for a given reaction must be known to complete this equation. A general form of the equation for the reaction rate for an autothermal reforming reaction using isooctane is

$$r_{C_8H_{18}} = dC_{C_8H_{18}}/dt = k \cdot [C_{C_8H_{18}}] \cdot [C_{H_2O}] \cdot [C_{Air}]^n \quad (18)$$

where k is the rate constant given by,

$$k = Ce^{(-E/RT)} \quad (19)$$

In this equation, E is the change in activation energy, C is the effective conversion frequency factor, R is the universal gas constant and T is the absolute reaction temperature. Thus, since A in the previous discussion is analogous to C_8H_{18} , r_A may be substituted by $r_{C_8H_{18}}$ therefore making the space velocity again a function of the temperature, the concentrations of water, air and fuel as well as pressure throughout the reactor. If one assumes a single step reaction, then the molar flow of both reactants and products may be calculated based on the conversion of isooctane. Unfortunately, there are several steps to the chemical reaction, which can potentially take place in various locations in the catalyst bed. Also, while the constants C, E, i, j and m are available for simple reactions, their determination for a reaction of this sort requires experimental investigation due to the catalyst dependent complexity of the kinetic mechanisms working in the reaction. It is important to note that while the reaction speed with temperature is unknown for isooctane using a catalyst, many elemental reactions will double their kinetic speed with each 10 degrees Kelvin increase in reaction temperature.³¹

Although the general trend is towards increased reaction rate with temperature, the global reaction may not follow this slope of reaction slope. so experimental testing of catalyzed reaction rates is necessary.

This is not a complete definition of the reaction since the interaction with the environment must also be taken into consideration. This is typically modeled by a steady state energy equation assuming changes in internal, kinetic and potential energies of the process are negligible. Thus a greatly simplified version of the energy equation includes effects due to flow, heat transfer, and the reaction since no work is completed in the reforming process.

$$- \dot{m} C_p dT + U(T_s - T)dA_p + (-\Delta H_{C_{8H_{18}}})(-r_A)dV = 0 \quad (20)$$

where ($\dot{m}$) is the mass flow rate, C_p is the average specific heat at constant pressure for the fluid mixture, U is the overall heat transfer coefficient, A_p is the circumferential wetted area, T_s is the temperature of the surroundings outside the tube and $\Delta H_{C_{8H_{18}}}$ is the enthalpy change due to the reaction. The specific heat was used in equation 20 for the change in flow energy or enthalpy. While the use of specific heat allows for simplicity and clarity in the equation, the calculation of the specific heat actually requires knowledge of the changes in specie fractions and temperature through the reactor for its proper use. The heat transfer term is simplified by the overall heat transfer coefficient, which involves resistances due to convection to the reactor walls from the fluid flow and conduction by the catalyst, conduction through the wall of the reactor and any insulation and finally radiation to the environment. The simplified version of the heat transfer energy is also specie dependent due to the velocity dependent convection coefficient. The reaction part of the equation involves the reaction rate as well as the heat needed for

the reaction to occur. This assumes a single step reaction, which is not the case for isooctane reforming. Thus each part of the energy balance is linked to the material balance by its dependence on the specie and temperature profiles through the reactor.

As a fluid passes through a catalyst bed for conversion, the interactions with the catalyst lead to a frictional pressure drop. A steady state momentum balance of the fluid may be used to calculate this pressure drop. Since the difference in the inlet and exit velocities were neglected in the energy equation, the density was assumed to be constant and there is no accumulation of mass in the system, momentum balance is just a force balance between the pressure drop and the friction, which yields

$$dP/dx + fu^2 \rho_f / d_p' = 0 \quad (21)$$

where x is the bed depth in the direction of flow, f is the friction factor, u is the axial velocity through the reactor based on the specie concentrations and the open area of the crosssection (also known as bed voidance), ρ_f is the density of the fluid and d_p' (6 times volume of catalyst/surface area of catalyst) is the effective diameter of the catalyst. For plug flow reactors, the correlation of Ergun may be used to find the friction factor (f)

$$f = (1.75 + 150(1 - \varepsilon_B)/\text{Re}') \cdot (1 - \varepsilon_B) / \varepsilon_B^3 \quad (22)$$

where the catalyst bed voidance (ε_B) and the Reynolds number (Re') are defined by

$$\text{Re}' = d_p' u \rho_f / \mu_f \quad (23)$$

$$\varepsilon_B = 1 - \rho_B / \rho_p \quad (24)$$

The bed voidance can be calculated using the bulk density (ρ_B = mass of the catalyst/total volume of container) and the particle density (ρ_p = pellet mass/pellet volume).

Since the temperature and product specie changes with bed depth, the friction factor, which is based on the Reynolds number, the fluid density and the axial velocity

will also be a function of bed depth. Thus, in order to solve the momentum equation, the temperature and specie concentrations must be known as a function of bed depth, which necessitates the use of both the material and energy balance equations. Fortunately enough, several experiments have been completed on the effect of pressure on plug flow reactors. Thus as a rule of thumb, pressure differences of less than 10 to 15% of the inlet reaction pressure are unlikely to effect conversion.³² Thus catalyst designers have investigated a variety of shapes in order to lower the overall pressure drop and thus attain higher space velocities without the effect of increased pressure on the reaction.

It is generally desired that ATR reactions occur near atmospheric pressure due to the increase of methane and higher hydrocarbons at high pressures. Also, lower pressure drop decreases the auxiliary power necessary to generate a given flow rate of fuel and air.

Unfortunately, the modeling equations are not in closed form for the temperature profile, the specie concentration profiles and pressure profile due to the lack of availability of catalytic reaction rate data and reaction mechanisms. Although the equations lack important information, they provided critical insight to the behavior of chemical reactors and thus were used with results from other experimental reactors and equilibrium calculations to design an autothermal rig.

Typically the efficiency and conversion results are compared to equilibrium conditions. Unfortunately, equilibrium dictates a nearly complete utilization of the fuel for the reactant fractions used, which may not occur due to catalytic and physical constraints. Since the efficiency as previously described includes the effects of conversion, another definition of efficiency is required to compare to equilibrium efficiency. Additionally, the previous equation for efficiency did not include the thermal

energy of the exhaust, which can be reclaimed for other processes. Thus the specific efficiency (η_{sp}) was defined in which the efficiency (η) was compensated for a lack of conversion and the energy contained in the exhaust.

$$\eta_{sp} = \frac{\eta_{Exhaust\ Compensated}}{conversion} = \frac{\frac{Energy\ out(H_2 + CO) + Effluent\ Energy_{T_{exit}-T_{in}}}{Energy\ in(Fuel)}}{1 - \frac{Energy\ out(Fuel)}{Energy\ in(Fuel)}} = \frac{Energy\ out(H_2 + CO) + Effluent\ Energy_{T_{exit}-T_{in}}}{Energy\ in(Fuel) - Energy\ out(Fuel)} \quad (25)$$

The exhaust energy was calculated as the energy difference of the products at the catalyst bed exit temperature and the reformer inlet temperature.

Specific efficiency allows for a better understanding of the efficiency of the catalytic process (and therefore the ratio of fuel burned to fuel reformed) without confusion due to conversion. Also, by removing the effect of conversion on efficiency, a better comparison may possibly be made to equilibrium efficiencies.

Autothermal Reformer Hardware Design Theory

In order to provide the best autothermal reforming environment, the reformer should be designed to conform to the assumptions of the equilibrium model and reduce kinetic limitations. Thus the reformer must be well insulated, use a catalyst with a small pressure drop at anticipated flow rates and provide the residence time necessary to convert the reactants. In order to facilitate design for the global reaction, three distinct sub-reactions can be assumed; combustion of the fuel with the air provided, the reforming of the fuel, and a water-gas shift (equations 8-10). These processes may be designed in three distinct zones: the combustion zone, the thermal zone and the catalytic zone. The

completion of each sub-reaction in its respective reaction zone is critical to obtaining the desired reaction products at the end of the catalyst zone.

Combustion Zone

In the combustion zone, fuel and air are mixed and burned to provide heat for the reforming reaction. The local temperatures evolved may top 2000°C, depending on the stoichiometry. Typically either a conventional flame burner or a catalytic burner is used to provide the heat.^{28,33} Burners have the advantage of fast reaction rates with potentially wide limits of heat generation. Although variable heat outputs are possible, problems with reactant mixing as well as soot generation can become concerns for the autothermal reforming process. Poor reactant mixing decreases heat generation by allowing unburned hydrocarbons to pass through the combustion zone. This can decrease the overall ATR conversion efficiency by decreasing the thermal energy available to reform the fuel. The added unburned hydrocarbons from the combustion zone must also be reformed, which compounds the effect of the lack of thermal energy produced by the combustion.

The varying local equivalence ratios caused by poor mixing may produce conditions conducive to carbon formation as well. The presence of carbon may decrease catalytic activity by blocking active catalyst sites in the catalyst bed (fouling) and potentially plugging the reactor. Carbon may be formed through several possible mechanisms.¹¹



The Boudouard and the fuel pyrolysis reactions can be averted through water addition, which lowers the partial pressure of CO for the reforming reaction. In practice,

a steam to carbon ratio of 2 to 3 is used to reduce carbon deposition with a margin of safety. Although the Boudouard reaction is reversible with water addition, the fuel pyrolysis reaction (equation 27) is not for higher hydrocarbon fuels ($n > 1$).²⁶

Beyond the local reactant concentrations, the global reactant equivalence ratios used in the combustion zone tend to be very close to the sooting limit for the fuel used in order to generate the maximum concentrations of the desired product specie. This region of combustion allows for direct heating and partial reforming of the hydrocarbons in the flame. The tendency to form carbon is again primary issue when the combustion zone is used in this fashion, thus along with air and fuel, water is typically required to reduce the CO fraction in the reformat. An effective method of introducing water into the combustion would be to mix the water and fuel before the combustion. Unfortunately, a fuel water premix generally provides inconsistent combustion.

Catalysts provide another method of heat generation. Catalysts used for combustion tend to provide combustion products in near equilibrium concentrations and typically have the capability to suppress carbon formation at what would be sooting air to fuel ratios in a conventional burner (below air ratio of 0.7 for isooctane).

There are several concerns with combustion catalysts as well. Combustion catalysts tend to have high minimum reactant inlet temperatures necessary for light-off (to begin combustion) for isooctane, which may require increased time for start-up. There are also limits to reaction temperature and reaction rate. The combustion of fuel and air in a combustion catalyst is a heterogeneous reaction based on the local equivalence ratios. This may create hot and cold spots within the catalyst bed and potentially melt (sinter) the catalyst. Thus, the bed may require thermal monitoring to

protect against over heating. Also, the volume of catalyst required for a given flow rate and heat release will vary depending on the catalyst manufacturer and must be designed into the reformer.

Thermal Zone

The thermal energy from the combustion zone may then be used in the thermal zone. While a portion of the reforming may occur in this zone, the primary purpose for the zone is to prepare the fuel and water reactants for the catalytic zone and pass on heat from the combustion to the catalytic zone. The additional fuel and water necessary for catalytic zone reforming may be injected into the combustion or provided in the effluent of the combustion section. In the former case, the combustion section is designed to operate in a fuel rich combustion regime, thus the thermal region allows unburned fuel and injected fuel to react with the water generated from the combustion. In the latter case, the burner operates near stoichiometry and fuel and water are injected in to the reactor after the combustion zone. Thus the thermal region in this configuration is primarily used for mixing.

It is vital to complete mixing of the reactants before entering the catalyst zone. Incomplete thermal or specie mixing can limit the ability of the catalyst to perform the reforming desired. Screens or porous plates may be inserted to trip the flow into a turbulent regime for mixing. Additional methods may include the use of injection nozzles, which require careful calculation of the momentum flux ratio in order to properly mix the steam and additional fuel into the combustion products. Unfortunately, this becomes quite difficult as the temperature and flow rate change under varying hydrogen demands.

Catalytic Zone

After passing through the thermal zone, the catalytic zone provides the final conversion of the reactants. Most ATR catalysts use nickel and precious metals although the actual formulation is typically proprietary.²⁸ The nickel typically used in autothermal reformers is known to catalyze both methods of carbon formation. Thus elements such as molybdenum and potassium may be added to the reforming catalyst. These elements have been effective in reducing the risk of carbon formation and crystal growth on the catalyst for commercial applications through elimination of the precursors to carbon formation such as polycyclic aromatic hydrocarbons (PAH).¹¹

Catalyst beds typically consist of catalyst-coated monoliths or high surface area structures (or substrates) such as pellets in order to allow maximum conversion (figures 17, 18). While pellets are manufactured in a variety of shapes, monoliths are commonly shaped in a honeycomb structure much like an automotive catalytic converter or foam.

Since the entire substrate is coated with catalyst, fuel conversion can occur on the outer surface of the structure although the majority of conversion is typically thought to occur within pores of the substrate due to the increased surface area for catalyst deposition. Thus, reactants convect to the outer surface of the structure to react or pass on through the pores through diffusion to active catalyst sites within. If reaction occurs at catalyst located inside the pores, the products of the reaction diffuse back out through the pores and convect back into the free stream flow (figure 19).

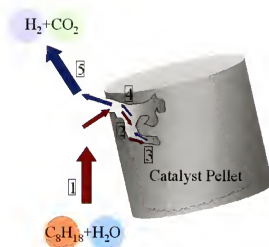


Figure 17: Monolithic catalyst bed



Figure 18: Various Pellet type catalysts

While pellets are designed to allow for maximum total surface area for catalyst by allowing reactant diffusion through its pores, monolithic structures tend to have a less developed pore structure, thus other methods are used to increase reaction rate.



1. Convection of reactants to catalyst pellet
2. Diffusion of reactants through catalyst pores
3. Reforming reaction
4. Diffusion of products out of pores
5. Convection back out to the free stream

Figure 19: Physical process of catalytic reaction on a pellet

Beyond reaching the structure, the correct fractions of reactants must be available at an appropriate temperature (catalyst dependent) in order to efficiently reform at the catalyst particle. Since the concentrations of the reactants vary through the bed, the reaction rate varies as well (equation 18). Due to the endothermic reforming reaction occurring through the bed as well as heat transfer losses, the temperature will tend to decrease with increasing bed length.^{18,25} Thus while the thermal zone may provide a homogeneous reactant mixture at an appropriate catalyst temperature, the catalyst bed for an ATR is not isothermal. Catalysts are designed to be most effective within a temperature range. Since there is a greater concentration of air and fuel at the beginning of the bed, the exothermic portion of the reforming reaction can locally dominate (if a combustion catalyst is used). This increases local bed temperature and reformer reaction rate, but may also sinter some of the catalyst. Catalyst sintering effectively reduces its surface area thus limiting its activity. Thus if a burner is used for heat, the distance

between it and the catalyst bed is of concern. At the exit of the bed, much lower fractions of air are available, thus the reforming reaction reduces the bed temperature. This lowers catalyst activity for the reforming reaction, but also may correspond to a lower equilibrium CO reformat fraction through the water gas shift reaction.

The temperature also varies within the structure itself. The increased structure surface area of a pellet promotes more reforming within the structure, thus a thermal gradient exists between the pellet center and its surface (figure 20). The reduction in temperature and reactant concentration reduces the effectiveness of a pellet towards its center. The thermal gradient is less for a monolithic structure due to a smaller pore depth and the conductivity of the substrate, which allows for a better distribution of heat through the substrate than pellets. This increase in heat at the reaction site increases the reaction rate for the catalyst and therefore typically allows for higher achievable space velocities.

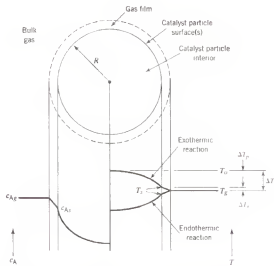


Figure 20: Concentration and temperature gradients within a catalyst pellet³²

With increases in space velocity, the thermal profile along the axis of the reactor would be expected to have less of a gradient. This increases the reaction rate through a larger portion of the bed, but provides less residence time in the catalyst. Although conversion typically decreases with increasing space velocity, the correlation is not direct.

Other variables such as the cylindrical aspect ratio (length/diameter) of the catalyst bed, gas channeling and catalyst condition are potential factors. As a rule of thumb, an aspect ratio of 3-5 to 1 (height/diameter) is considered optimal for pelletized bed designs, but this changes based on the type of catalyst used.³² Even with an appropriate aspect ratio, gas channeling may lower the overall conversion. Gas channeling occurs when the reactants find a path around the catalyst in a catalyst bed, therefore avoiding the effect of the catalyst (figure 22). Catalyst shapes are typically designed to reduce this effect as well as to reduce heat transfer limitations within the pellet.

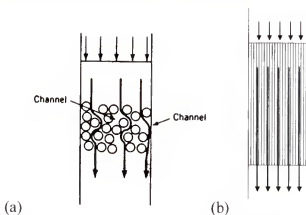


Figure 21: Gas channeling in a catalyst bed packed with pellets (a) and with monolith (b)

Channeling is designed into a monolithic structure although the channels are typically small and long enough to react the specie effectively. The monolithic design also allows for a reduced pressure drop as compared with pelletized beds.

Sintering, chemical coating (fouling) or a chemical deactivation can limit active catalyst surface areas and reduce activity. Catalyst sintering may occur by the improper heating of the catalyst by the combustion section. This outcome may be averted by careful control of the air and S/C ratios. Unlike sintering, catalyst fouling involves a chemical coating of the reaction sites. As the reactants form the products at the catalyst particle, several chemical intermediates are formed. These intermediates may adsorb to the catalyst surface until enough energy is supplied to remove the intermediate and continue the reaction. The space the intermediates occupy limits area necessary for new reactions to take place and in effect coats the catalyst. This effect is known as fouling. Fouling may also occur from high-energy pollutants in the fuel stream such as oils and higher hydrocarbons. Experiments have shown that fouling and chemical deactivation tends to be less problematic with increased processor temperature.²⁵

While catalysts may recover activity from fouling, catalyst deactivation is permanent. The catalyst can be deactivated (poisoned) if a strong bond forms between the catalyst and a chemical, thus creating another (less active) specie. Sulfur and chlorine are notorious for poisoning catalyst beds at low (ppm) levels and thus must be eliminated before entering the catalyst bed.^{24,25} New catalysts are being developed, which have increased resistance to the effects of sulfur although generally, the chemical must still be removed before entering the fuel cell stacks designed for transportation applications.

An additional catalyst concern is activation and storage. Some autothermal catalysts require 30 hours or more at operating temperatures (600°C-800°C) to reduce from their oxidized storage state. Also in normal operations, once reforming has stopped, the catalyst may be required to remain in an oxygen free environment in order to stay in

an active state for the next run. For automotive applications, this necessitates stowing another container (of inert gas) for fuel cell engine storage. The use of precious metal catalysts eliminates the need for an alternative environment for storage and the time necessary for activation, but the precious metal also dramatically increases the cost of the catalyst.

Adjustments to the catalytic formulation also allow the combustion and thermal zones to be combined into the catalytic section by adding a combustion component to the reforming catalyst. This method allows for less heat transfer losses than other methods of heat integration due to the proximity of the sections and is typically used in autothermal reformers. The catalytic mixture for this to occur unfortunately does little to reduce light off issues with combustion portion of the catalyst, although several methods may be explored for fast start-up.^{34,35}

Previous Experimental Autothermal Reformer Investigations

There have been several articles outlining the results of various investigations into the autothermal reforming of gasoline. Epyx (a fuel processor company) has demonstrated reformat hydrogen and CO concentrations of greater than 43% and less than 0.5% respectively for a 20 kW_e autothermal reformer for 600 hours of operation on pump grade gasoline. While acceptable for PAFC use, PEMFCs require less than 100 ppm CO and thus another CO polishing unit is required for their unit. They found that the air/fuel and steam/fuel ratios were critical variables to the desired output specie fractions.¹⁹

Doss completed a theoretical parametric analysis of the fuel processor and total system performance by varying the operating pressure, reforming temperature, water to fuel and air to fuel ratios, electrochemical fuel utilization, and thermal integration of the

fuel cell stack and fuel processor subsystems.³⁰ He found that reforming temperature is a significant variable to determining equilibrium reformer product concentrations. Higher reforming temperatures lead to lower hydrogen concentrations in the reformat while increases in the steam to carbon ratio reduce CO content. Lower reforming temperatures (below 827°C) lead to the formation of methane which lowers the amount of hydrogen in the reformat. It can be gathered from his research that as pressure increases, the concentration of CO decreases. Also, he calculated that the efficiency of the reformer increases with increasing reactant temperature although 627°C was used for most of the calculations.

Gasoline is a very complicated sulfur bearing mixture of fuels, thus a known gasoline equivalent is typically used. An analysis similar to Doss was completed by Docter using the German gasoline equivalent C_7H_{12} (Normalbenzin).²⁷ He found similar results to Doss, but used an adiabatic rather than an isothermal equilibrium model. Due to this change, he was able to find the air ratio necessary (0.28) for high conversion with inlet reactant temperatures of around 500°C for water and air respectively and a reaction temperature of 830°C. It was also found that by reducing the preheat temperatures by 200°C, which was more achievable in an integrated fuel cell system, the theoretical efficiency was reduced by 3% and the reaction temperature decreased by 30°C. He also surmised that the increased efficiency from the higher inlet temperature was due the decreased amount of fuel burning necessary to support the reforming reaction. Thus more fuel is simply steam reformed from the inlet reactant heat.

Wieland performed equilibrium calculations on a hydrocarbon feed similar to Docter and found nearly the same optimum points of operation as Docter. Wieland went

on to build an autothermal reformer to test the equilibrium calculations and found good correlation between the theoretical and experimental trends in the products.²⁸ Moon also built an autothermal reformer, but used isooctane (another gasoline equivalent) as the fuel.³⁶ While Moon used commercial naphtha reforming pallet type catalyst, Wieland used a proprietary monolithic catalyst. The enhanced heat transfer in the monolithic catalyst allowed for a space velocity of between 30000 and 60000 while Moon used a gas hourly space velocity of 8776 for the majority of his experiments. In fact, space velocities of up to 100,000 have been reported using monolithic catalyst.³⁷

Problem Statement

It has been theoretically shown that an increase in inlet reactor temperature increases the total moles of hydrogen and CO in the reformat, but no such study has looked into the experimental effects of the inlet temperature on bed temperature, fuel conversion or possible space velocity nor given experimental support for the effect of inlet temperature on the efficiency.

Equilibrium calculations have shown that an increase in inlet temperature also increases the reaction temperature. This may allow for a higher space velocity at a similar conversion percentage due to higher catalyst activity. Also, since in theory, most of the reforming in a catalyst bed occurs near the entrance due to combustion energy available at this point, the inlet temperature should have a significant effect on efficiency and conversion of the fuel. Unfortunately, the inlet reactant conditions and the catalyst volume typically define the space velocity, thus an increase in inlet temperature at the same mass flow rate will also increase the space velocity. This increased space velocity may reduce the potential benefits of increased efficiency and faster reaction rate due to the shorter residence time and thus potentially lower total fuel conversion.

Thus the intent of this discourse is to experimentally separate the catalyst dependant effects of inlet temperature from the definition of the space velocity and potentially enhance the definition of the space velocity as well as to examine the dependence of efficiency and conversion on inlet temperature. Since efficiency is theoretically dependent on conversion, the specific efficiency will be used instead in order to separate the two dependent variables. Finally this work will facilitate the design and operation of an autothermal reformer, by creating an analytical tool to help predetermine possible reformer performance with the additional variable of inlet temperature.

CHAPTER 3 AUTOTHERMAL REFORMER DESIGN

In order to test the selected dependent parameters, several independent parameters must be controlled. These parameters include the reactant inlet temperature, the total flow rate through the catalyst bed (space velocity) and ratios of the reactants (air/fuel and fuel/water ratios). Thus an experimental apparatus was designed and constructed to analyze the independent parameters affecting the bed temperature, specific efficiency and conversion of an autothermal reformer.

Previous Reactor Designs

There are several organizations and companies that have built fuel processors using autothermal reforming.³⁸ Many of the processors were designed to place all sections of the fuel processing system into a single device while others have taken a more segmented approach.^{36,39,17,40} More specifically, the autothermal reformer portion of the fuel processor was typically described as a refractory lined pressure vessel into which fuel, water and air were injected. Most designs employed catalytic combustion over a packed bed just before entering the catalytic zone. The actual make-up and structure of the catalysts varied although the primary component of the conversion catalyst was nickel. Beyond these facts, information on autothermal reformer design or on any testing apparatus was extremely limited.

The University of Florida Autothermal Reforming Rig

Using this information, a 30 kW thermal autothermal reformer and a corresponding test rig were designed and built by the University of Florida Fuel Cell Research and

Training Laboratory. The rig itself was designed for flexibility. It allows for future study of the effects of several aspects of autothermal reforming such as reactant feed ratios and temperatures, fuel choices, changes in the space velocity, catalyst type and shape, container geometry, and other fuel processor concerns.

In order to gather data required for the present investigation of effect of inlet temperature as well as to allow for operational simplicity, the reforming rig was built in sections. They include reactant supply, reactant flow, reactant conditioning, reforming, exhaust, sample conditioning, sample collection and control (figure 22).

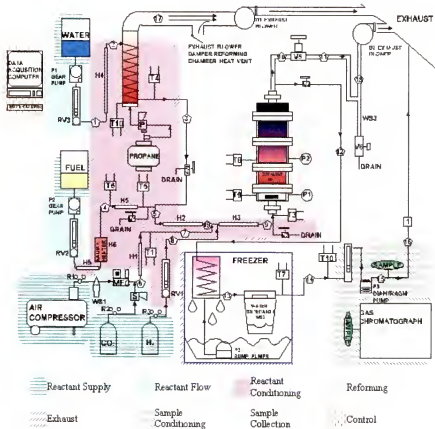


Figure 22:Rig flow diagram

Reactant Supply Section

The reactant supply section provided storage of specie needed for the start-up, shutdown and operation of the reformer. These specie included water, fuel, air, hydrogen and carbon dioxide. The liquid specie were stored in separate vessels (5 liter for isooctane and 7 liter for water) and were placed on scales (0 – 5 kg rating) for a measurement of average mass flow over the experimental period. Each of the chemically resistant plastic containers employed a shut-off valve and a cap to ensure specie purity while in use. Due to the vapor pressure of the fuel, it was removed from the storage vessel and stored in a glass vessel when not in use. Additional plastic storage tanks (5 liter) were used to store extra water for elongated run times.

Water for the experiment was supplied by filtering and deionizing tap water. This was necessary due to the volume of water needed for the experiments as well as the chlorine and other possible specie present in conventional tap water. Chemical grade isooctane was purchased from a supplier for fuel (appendix F). A plexiglass shield was erected in order to contain any reactant spillage or splatter from the liquid transfer of the reactants in the supply section.

An oil free air compressor with a 20-gallon tank was used to continuously supply pressurized air for the reformer (appendix F). Although the compressor included a pressure regulator, which provided a rough estimation of the pressure, another manual regulator was placed on the air line to ensure the proper pressure at the mass flow controller. Hydrogen was also required for the reformer. Since a monolithic catalyst bed with precious metal content was chosen for the experimentation, the catalytic combustion of hydrogen was needed to increase the catalyst bed temperature to the light-off temperature for isooctane (400°C). Hydrogen was chosen because it easily combusts

over the catalyst at ambient temperatures, the product of the reaction does not affect the catalyst bed itself and it has a wide range (4 – 76% by volume in air) of combustible fuel fractions. Thus varying the fuel only can control heat introduction to the catalyst bed. Carbon dioxide was also necessary to purge the reformer of combustion gases for shut down and for safety purposes. It was equipped with a normally open solenoid valve in case of emergency. The carbon dioxide and hydrogen were stored in typical laboratory compressed gas cylinders with pressure regulators (appendix F). The cylinders were also belted to the building for safety. While any inert gas may be used for purging, carbon dioxide was used because it had no previously stated effect on the catalyst and has more capacity than other inert gases of similar price. Air was not used for purging since increasing airflow through the catalyst bed tends to produce a hotter reaction in the catalyst bed and thus can sinter the catalyst rather than quench it.

Reactant Flow Section

These reactants were then fed through tubing to the reactant flow section. The reactant flow section acted to give real time quantifiable flow rates of the reactants. Both water and isooctane flowed from their designated tanks to separate stainless steel gear pumps and then through calibrated rotameters for flow metering.

Since the air compressor used ambient air, which may have contained a significant fraction of water, air from the compressor was directed through a water separator and then a desiccant before being regulated by a mass flow controller (MFC). Water separation proved to be critical for the mass flow controller since injection of only small amounts of liquid water were enough to fool the MFC sensor into allowing its maximum flowrate (30 liters per minute) thus potentially sintering the catalyst. When wet, the

malfunction of the MFC was alleviated by using heat to dry the device. The MFC was calibrated using an online manometer to ensure correct flows through experimentation.

Reactant Conditioning Section

Once the reactants were properly metered in the reactant flow section, they proceeded to the conditioning section for heating to prescribed temperatures before entering the autothermal reformer. Both air and isooctane feed flows were heated using electrical heat tape (312 watts for air and 468 watts for isooctane). The heat tapes required temperature monitoring to ensure operational temperatures were below the maximum (760°C). Thus several surface temperature thermocouples were installed to check the temperature of the heat tape. This proved to be difficult since the high temperature (1260°C) insulation that was necessary for optimal heating could not be applied evenly, the heated tubing was not always straight and the flow inside increased in temperature after entering the heated section of tubing. These factors produced unexpected hotspots in the tape, which resulted in heater burn out. Through strategic placement of thermocouples and regulation of the maximum temperature those thermocouples experienced, heater burn out was reduced.

While air and isooctane could reach their prescribed temperatures using only temperature monitored heat tape, the volume of water required for autothermal reforming of isooctane required more thermal energy than was possible to easily implement using heat tape. Thus a propane burner was used to vaporize the water while a series of electrical cartridge heaters were used to superheat the water to a set temperature. A 37 kW turkey fryer burner was used to combust propane through a 4-inch stainless steel tube. Stainless steel spacers were placed between the burner and the tube to allow visual inspection of the flame, check combustion temperature and to allow for additional air for

flame initiation. Although additional air was required to start combustion, air during operation was sucked in through a throttle on the burner, which was adjusted for the to ensure a flame throughout testing. Heat was exchanged from the burner to the water though a quarter inch copper coil inserted in the hot gas flow. The stainless steel combustion tube was insulated to reduce heat loss, keep from burning insulation on wires and to reduce the burn risk to the operator. An outdoor grill propane tank located in a cage outside the lab fed the burner. The gas flow itself was controlled through a proportional valve near the burner.

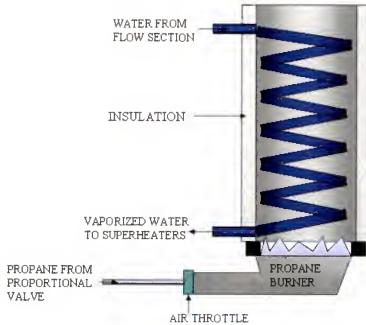


Figure 23: Water vaporizer schematic

After being vaporized by the propane burner, superheating of the water flow was accomplished through a series of controlled stainless steel sleeved high temperature (870°C) cartridge heaters placed in the water flow (figure 24). This was necessary since the thermal resistance in even thin walled (0.016 inch wall thickness) stainless steel tubing made heat tape ineffective. The design proved to be so effective that high

temperature insulation was not needed. The lack of thermal insulation allowed for visual inspection of overheating of the cartridge heaters and thus also the existence of the water flow. Although a portion of the fitting was in direct contact with the heater for sealing, the temperature rating of the fitting was comparable to the maximum temperature of the heater and thus the fitting did not leak. Two 5 inch long 400 watt cartridge heaters were used in conjunction with two 10- inch long 600 watt cartridge heaters to superheat the water flow to over 400°C for autothermal testing (figure 24).

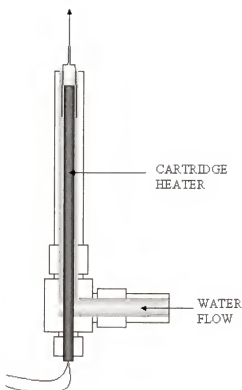


Figure 24: Water superheater design

The temperature of superheat of the isooctane and water flows was allowed to increase for start-up without affecting the catalyst bed by directing the flows to valved drains on each line, which exhausted to atmosphere, bypassing the catalyst bed. Beyond

the vaporization test valves, the reactants were mixed prior to injection to the reformer by two stainless steel union crosses (figure 25). The first cross mixed steam and isooctane whose mixture was passed to the second cross which introduced air and hydrogen into the stream and passed the final mixture on to the reformer. The additional port on the first cross was used as a drain should condensate form in the reformer or in the tubing leading up to the reformer. In order to prevent condensation in the reactant mixing portion, additional heat tape was used. A thermocouple was placed after the mixing of the reactants and before entering the reformer in order to acquire the independent variable of reactor inlet temperature.

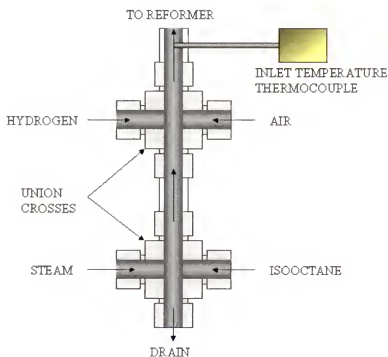


Figure 25: Mixing design

This location was chosen since the location just before the catalyst bed was not as controllable as before the reformer due to the effects of radiation from the bed. This allowed any heat losses in the reformer before the catalyst bed to be assumed part of the experiment.

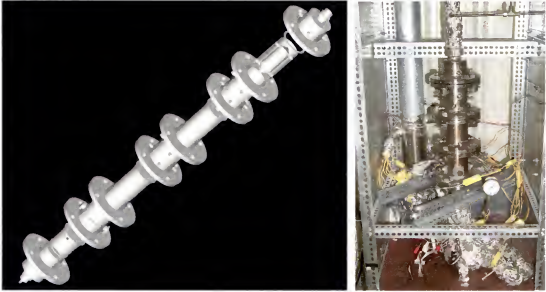


Figure 26: Professional Engineer rendering and picture of the completed reformer inside the rig housing

Reforming Section

After conditioning, the reactants entered the reforming section (figures 26, 27). The reformer was designed as five flanged all stainless steel sections: burner, fuel and water input, mixing, catalyst bed, and exhaust. Each part was dedicated to a particular function of the previously described reforming process and designed to allow individual analysis. Each section of the reformer was built using a thin walled (0.07 inch) three inch diameter tube placed inside a three inch pipe as internal and external sleeves respectively to protect against wall heat transfer losses and thus to reduce potential start-up and shutdown times. Finally, in order to ensure proper containment, the reformer each

section of the reformer was bolted together and sealed using high temperature flange gaskets (450°C).

Burner Section

Upon entering the reformer, a perforated plate within the burner section was implemented to complete a final mixing of the specie. The temperature and static pressure of the flow at this point were observed using a thermocouple and a bourdon tube gauge though a couple of the many 1/8th inch ports that line each section. The burner section was also designed for insertion of a 1/8th inch NPT glow plug just above the perforated plate for POX operation of the reformer although another burner section was built which may have been more appropriate if POX operation was desired.

Injection Section

The flow then proceeded to the fuel and water injection section. The injection section has four large 3/4" NPT ports allowing the possibility of using a variety of methods of injection. The injection section was also designed as a void into which various mixing schemes such as swirl vanes may be applied. Injection of fuel specie after combustion allows for testing in the POX configuration. A dedicated mixing section was also added just after the injection section to allow for in situ mixing analysis. For the current autothermal reforming study the catalyst bed was relocated to the injection section to reduce wall heat losses and thus limited specie condensation before entering the bed.

In order to ensure limited heat loss in this section, the cylindrical catalyst coated monolith bed used was wrapped with 1/32 inch thick high temperature insulation (1260°C

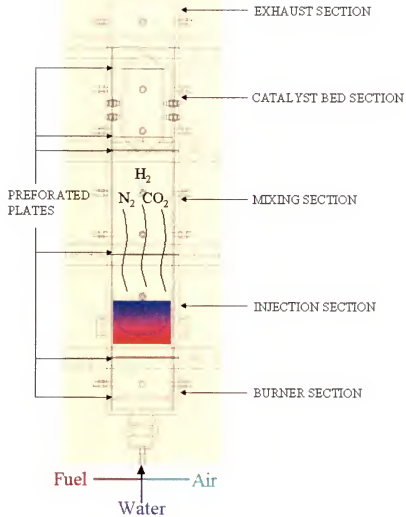


Figure 27: Overview of reformer sections

maximum temperature) to fit into the stainless steel sleeve. In order to guard further against wall losses and to ensure all reactant specie was directed through the catalyst bed, the area between the inner sleeve and the pipe was also filled with high temperature insulation (figure 28).

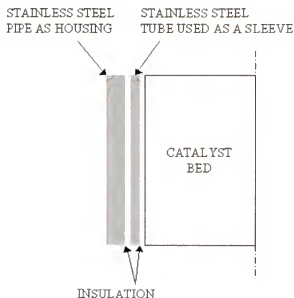


Figure 28: Use of insulation in catalyst bed section of reformer

The catalyst itself was a mixture of nickel and magnesium oxide as well as other proprietary materials, which was applied to a ceramic monolithic substrate in the form of a channeled honeycomb similar to a catalytic converter for a conventional automobile. Since a monolithic substrate was used instead of the pellet type, temperature probing from the side of the catalyst bed, which was common in pellet type designs, required drilling of the catalyst bed. Thus the temperature through the catalyst bed was found using very thin (0.020" diameter) thermocouples, which were inserted through the pores of the honeycomb catalyst structure at varying depths (figure 29). The entrance of the bed had the highest concentration of thermocouples since it was assumed that this region would have the greatest temperature gradients of the bed. The thermocouples were introduced by placing all the thermocouples through a single 1/8th inch port, which was sealed from the outside with silicone. A rough calculation of the force imposed on the thermocouple head by the fluid flow was completed on the thermocouple to ensure that the thermocouple movement within the catalyst bed would be minimal.

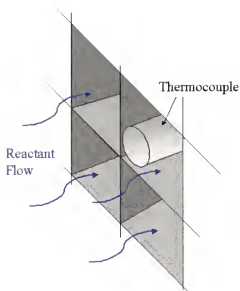


Figure 29: Thermocouple placement in catalyst flow field

Only the axial temperature distribution was taken since it was assumed that the velocity and specie profiles for all channels through the catalyst bed were the same and thus the thermal profile radially through the catalyst bed was constant.

Catalyst Bed Section

Although the catalyst bed was relocated to the injection section of the reformer for testing, the catalyst bed section was designed for pellet type substrates to reduce the volume of catalyst required for a 3 - 5 to 1 aspect ratio with a limited increase in pressure drop. The section allowed for future testing of catalyst beds as small as 150 ml. In order to keep the pelletized bed in place during operation, two additional perforated plates may be implemented. Finally, this section also allowed for temperature and specie sampling through a plurality of 1/8th inch ports.

Reformer Exhaust Section

Finally, the exhaust section of the reformer reduced the diameter of the reformer for transport of the reformat to the rig exhaust section. This was completed through a 1

inch NPT union coupling, which allowed for quick removal of the reformer from the exhaust system. It as well had several 1/8th inch ports for sampling.

The entire reformer was supported from both the bottom and top by a rig housing to allow for ease in the replacement of a single section. The rig housing was made of steel elbow brackets with sides of aluminum sheet for safety and bottom of steel sheet for structural strength. The rig housing also contained the reactant conditioning section of the rig for safety purposes.

Sample Conditioning Section

The reformat then exited the reformer and proceeded either to the exhaust or the sample conditioning section. If an analysis of the reformat was desired, the reformat was passed through a freezer fitted with a condenser and a water separator to remove as much of the fluid as possible. The condenser consisted of a coiled $\frac{1}{4}$ inch copper tube placed in a container fed with freezing water provided by a sump pump at the bottom of the freezer. The water from the sump pump was directed into the bottom of the condenser container providing counter flow heat exchange with the tubing after which the heated water poured out of the top of the condenser and fell through the air in the freezer to cool much like a cooling tower. The sump pump was also used to evacuate the freezer of water when experimentation was complete. After passing through the condenser, the liquid was separated using a conventional home water filter housing. Since isooctane was less dense than water, a conversion could be found through visual inspection of the liquid specie with a graduated cylinder. Due to the possibility of fuel and water vapor passing the water trap, a thermocouple was employed to determine the vapor pressure and thus the total water and fuel passing the trap.

Sample Collection Section

After conditioning, the “dried” sample entered the sample collection section where it flowed through a flow meter, a variable suction sample pump, a sample collection point and a one-way valve before being directed towards the exhaust section. The factory calibrated flow meter and a thermocouple were used to calculate the sample flow rate. An oil free suction pump was used to pump the sample through sample conditioning section to the sample port. The one-way valve provided backpressure for sample collection and kept other down stream specie from affecting the sample.

Exhaust Section

The exhaust section used two high-temperature (maximum temperature of 315°C) suction blowers to remove both propane combustion and reforming products from the experimentation area. The two exhaust lines were kept separate to reduce the chance of combustion of the reformat. In order keep a combustible equivalence ratio in the propane burner, variable suction dampers were placed on the propane burner exhaust in the reforming box and in the lab area. In effect these dampers decrease the suction of the blower on the burner thereby allowing an appropriate amount of air to flow into the burner for combustion. Also, by placing the dampers in the reforming box and in the lab area, any other gaseous specie, which may have leaked from the rig, may also be exhausted.

While the propane exhaust line used conventional duct work, the reformat exhaust used a 1 inch steel pipe from the reformer directly to its blower. The condensable specie in the reformer required that the pipe leading from the reformer be insulated to limit this effect until the height of the blower was reached. In order to reduce the probability of condensate reentering the reformer from the exhaust, a valved drain port was drilled in

the pipe just after the exit of the reformer. A back pressure valve was placed on the reformat exhaust line to study pressure effects of the reforming process and to drain specie from the reactant streams through the drain on the bottom of the mixing portion of the reactant conditioning section. In order to guard against overpressure, a blow-off valve set to 30 psi. was installed that circumvented the backpressure valve. The reformat exhaust line was also tapped for the return of the excess sample specie from the sample collection section. Due to the cooling in the reformat line, significant liquid from the reformat formed thus a water trap was built before the blower in order to allow for proper operation of the blower. Both exhaust lines were hung from the ceiling of the lab. Each blower had individual stacks, which exhausted outside the building and above the nearby roof. The stacks were topped with caps to reduce the collection of rainwater in the system.

Data Acquisition

Acquisition of gas fraction, volumetric flow, pressure and temperature data were necessary to determine the dependent variables of each experiment. In order to find the hydrogen and carbon monoxide gas fractions, both a thermal conductivity detector (TCD), which was located within a gas chromatograph (GC) and a hand-held Non-Dispersive Infrared (NDIR) analyzer were used. The hand-held device used NDIR to measure CO while other electrochemical cells were installed to measure CO₂, O₂ and NO_x content. The TCD was calibrated using various mixtures of CO₂ and H₂ to identify the hydrogen fraction. The NDIR operates on the concept of the absorptivity of various gases to infrared. It completes this by matching a pre-calibrated intensity plot with wavelength to an actual plot generated by the sample gas, a regulated infrared source and an optical block which transforms an intensity into a voltage within the temperature

controlled device. The GC used a mol sieve maintained at 100°C to physically separate gaseous specie over time. The separated specie were then directed to the TCD, which registered a potential difference across a Wheatstone bridge by flowing the separated specie in the sample across one of the resistors in the circuit and a known carrier gas across another.

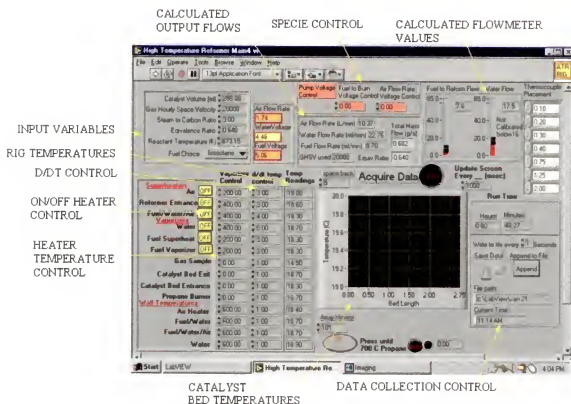


Figure 30: Program front panel

While pressure gauges and graduated cylinders measured the pressures and volumes, a LabView based user interface was designed for the reforming rig to control heaters for vaporizing and superheating reactants and to give the experimenter a temperature analysis of the rig. K-Type thermocouples were placed throughout the rig to give vaporization and superheat information for the reactants as well as temperatures

throughout the reformer. These signals were fed through a thermocouple module, which transformed the millivolt thermocouple readings into a voltage that the computer could read. These temperatures were shown on the front panel of the user interface and updated every second. Of the many rig temperatures, the reformer bed temperatures were fed to a graph for visual interpretation. The program allowed for faster acquisition although 1 sample per second was used to limit data storage.

The temperatures acquired from the rig were used to control the vaporizers and superheaters. The program then sent out a signal to a digital output module, which controlled relays that switched power to the heaters depending on set point temperature.

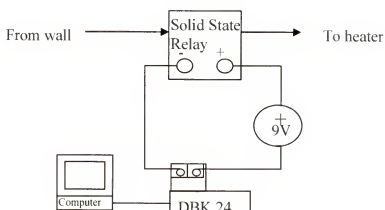


Figure 31: Digital output module hook up for heater control

A heating control to provide controlled temperature increase with time (dT/dt) was implemented for several heater and thermocouple combinations. This allows the user to limit the rate of temperature change experienced in both heating and cooling for the reactant conditioning section, and acted to damp out many of the temperature oscillations seen through the data acquisition system.

The probable voltages required for all pumps and the mass flow controller for a given air ratio, S/C ratio, fuel type, catalyst volume and space velocity were calculated in

the program based on several input parameters. The flow rates for the reactants were also displayed on virtual flow meters in the program, which corresponded to what should be seen on the actual flow meters. Although computed, the actual flows were controlled manually either by input to the program in the case of the air flow rate or through physical manipulation of power supplies for water and isooctane. Since the air flow was an important factor in catalyst bed temperature, the control of the air flow was limited to 0.2 volts (or 2 liters per minute) above the calculated air flow. This proved to be vital as errors in the manual input of flow voltages occurred.

The proportional valve for the propane burner was also controlled through the program. Computer control was required for the proportional valve to guard against flameout and to throttle the propane between low and high settings for additional control of water superheat temperature. Both the air mass flow controller and the proportional valve were controlled through an analog output module. Control of the fuel pump was also programmed for the analog output module although not used since another type of pump requiring higher current input was desired.

Safety Devices

There were several additional devices, which aided in the safe operation of the rig. Should a fire occur, CO and soot detectors were strategically placed on the wall above the rig structure and in the center of the ceiling. The rig area was also equipped with a chemical type fire extinguisher, which was placed at the doorway between the control room and the lab area for emergencies. Since hydrogen combustion has a colorless flame, a high temperature alarm was installed in the rig housing to ring in the control room. There were two emergency switches; one located in the experiment area and one in the control room which turned off all power to the reactant supply section,

vaporizers and superheaters and allowed CO₂ to flow through the fuel processor. The windows of the control room were covered with Lexan for explosion resistance. Finally, the entire lab was exhausted using a large overhead blower to lower the possibility of collecting potentially hazardous concentrations of gases in the lab.

Rig Operation

In order to prepare for the start of the rig, the supply of all reactants (air, isooctane, water, propane, CO₂) was checked, overhead and exhaust blowers were turned on, the high temperature alarm was initiated and the control program was started. After this, air and hydrogen were used to preheat the bed to 350-400°C (light-off temperature for isooctane). Once the bed reached 350-400°C, the heaters and the propane burner were used to vaporize water and fuel. Once vaporized, the fuel was introduced to the catalyst bed with the air and hydrogen. This typically made the temperature begin to increase dramatically, after which the hydrogen was turned off and the vaporized water was directed into the bed to reduce the temperature.

In order to take a data point, steady state operation for a given set point must be reached. This occurred when the product specie concentrations from the on-line gas analyzer and the bed temperatures stabilized. After reaching steady state, a 20-minute trial started by noting the total fuel and water masses used over the trial and the volumes of water and fuel accumulated in the sample conditioning water trap. Once the contents of the water trap were measured, the gas sample volume fractions from the on-line analyzer were tabulated, a sample for the GC was taken and water trap was cleaned and the trial was restarted if desired.

For shutdown, both water and fuel flows were stopped and all heaters were shut off, while carbon dioxide purged the reformer and dropped the temperature (see appendix F for a detailed procedure of the start-up, operation and shutdown procedures).

The data collected from the rig were then processed to calculate the specific efficiency and conversion for the run. In order to complete this calculation the sample flow rate was found using the gaseous water and fuel fractions passing the water trap as well as the hydrogen, CO, CO₂, O₂ and NO_x fractions and the temperature and pressure at the flow meter. Once the flow rate was found, the total mass of each gaseous specie could be found and added to the mass of fuel and water in the water trap. This gave total mass fractions for the reformer and thus conversion of fuel and specific efficiency with the mass of reactants (see appendix B for detailed calculation).

Experimental Test Plan

A testing strategy was required to show the effect of increased inlet temperature on the specific efficiency and percent conversion. Unfortunately not all of the theoretical design space could be examined experimentally due to limitations in the experimental set-up. Although isooctane had not been studied on a catalyst bed of this type, the manufacturers stated that it was designed for a maximum space velocity of around 30,000 and a S/C ratio of no less than 3 for proper operation. A 400°C set point was chosen as a maximum inlet temperature according to catalyst manufacturers suggestions. 300°C was used as the lower set point temperature to provide a theoretical efficiency difference, which was significant (3% at a steam to carbon ratio of 3). It was found through experimentation that space velocities as low as 25,000 at the preheat temperatures previously mentioned could still yield quantifiable fuel in the products. Thus the extents of the space velocity were set between 20,000 and 25,000, which corresponded to

manufacturers recommendations. Since thermodynamic equilibrium concentrations of CO and H₂ decrease for increasing S/C ratio at this inlet temperature, only a S/C ratio of 3 was used. Finally, using equilibrium calculations, the optimum air ratio for a S/C ratio of 3 theoretically varied between 0.26 and 0.29 for these inlet temperatures. It was discovered experimentally that the catalyst bed was not capable of efficiently converting the fuel in the previously stated range of equivalence ratios and space velocities and thus the range for the air ratio was changed to between 0.608 and 0.672. Unfortunately the increase in air ratio decreased the maximum possible adiabatic efficiency to between 31 and 38%. This range was consistent with other experimentation on this catalyst type and still allowed for a quantifiable conversion difference.⁴¹ Using these constraints, new extents of the independent variable space were chosen.

Table 1: Settings for factorial experimentation

	Low (-)	High (+)
A/F Ratio	0.608	0.672
Space velocity	20,000	25,000
Temperature	300°C	400°C

In order to cover this design space, a 2^k factorial experiment design was implemented. This design is typically used to statistically relate the effects of various independent parameters on a system and provide a working model for the system operation with the least number of trials. This type of experimental design tests only the highest and lowest limit of each independent variable range and assumes a linear relationship between each independent variable and the systems dependent variables.

In order to validate the model, points between the extents of each variable must be taken. Since three independent variables were chosen for study on their effects on conversion and total power output, a 2³ factorial experimental design was performed.

This yielded eight configurations of high (+) and low (-) levels of the three variables. An input matrix was made in order to ensure that all combinations of the variables were run.

Table 2: Factorial matrix run order

A/F Ratio	Inlet Temperaure	Space Velocity	Run Order
+	+	+	15,10,24
-	+	+	19,4,16
+	-	+	9,13,6
-	-	+	2,21,5
+	+	-	1,8,23
-	+	-	3,22,12
+	-	-	14,11,7
-	-	-	18,20,17

The runs were also randomized in order to limit the effect of variables not considered in the analysis on the dependent variables. Several iterations were completed for each configuration in order to allow for statistical analysis and identification of outliers. After taking an average of the three runs in each configuration, the effects (E) and interactions (I) of each variable on the efficiency, conversion and bed temperature were found.

$$E_i = \sum X_i Y / 4 \quad (28)$$

$$I_{ijk} = \sum X_i \times X_j \times X_k \times Y / 4 \quad (29)$$

where X_i is the map of each variable in the space -1 (-) and +1 (+) as indicated by the two tables above. (tables 1, 2) The significance of each effect or interaction was also calculated by comparing a form of the error in the effect or interaction to a level of expected noise for the number of trials taken (see appendix d for significance calculation).

CHAPTER 4

RESULTS

It is important to note when conveying the results that although the results were an indication of the reaction characteristics for an automotive scale autothermal fuel processor, the fuel processor was neither optimized for maximum conversion, nor efficiency. Also, the results were specific to the catalyst type and geometry used. Changing these additional variables will change the results. While not optimized, the experimental results of varying the independent parameters indicated several trends, which may aid in the further optimization of reformer operation.

For each run, nine bed temperatures were acquired to analyze temperature change, and the specific efficiency and conversion were calculated. These three dependent variables were chosen to show the effects and interactions between the independent parameters of air ratio, inlet temperature and space velocity. It is important to note that the results were indicative of testing within the previously described ranges and thus trends formed from the experiment may not hold outside the experimental ranges (table 1).

Bed Temperature Results

In order to compare the effects of the independent variables, an overall average bed temperature and standard deviation of the mean temperature was calculated for each configuration where AR is the air ratio, IT was the inlet temperature and SV was the space velocity (table 3).

Table 3: Average bed temperature for each configuration

Configuration (AR, IT, SV)	Average Temperature (°C)	Standard Deviation of the Mean
-, -, -	592.65	33.59
+, -, -	607.12	34.35
-, +, -	613.15	35.18
+, +, -	620.34	34.81
-, -, +	597.48	38.34
+, -, +	616.46	35.04
-, +, +	618.09	27.85
+, +, +	629.40	27.57

While the average bed temperatures were within 37°C of each other, there was a large spread in the data indicated by the standard deviation of the means. It can be seen that the lowest average temperature occurred with the low setting of all the independent variables while the highest average temperature coincided with the high setting of all independent variables. A similar trend did not exist in the standard deviation of the means.

In order to further explore temperature differences caused by the independent parameters, the average axial bed temperatures for both high and low settings for each of the parameters were plotted. The average uncertainty of the axial temperature plots was applied as error bars on the graphs of the catalyst bed temperature to give an understanding of the significance of the temperature difference based on each effect. The uncertainty was calculated using the standard deviation of the mean for each thermocouple in the bed for runs in each configuration, multiplying by a factor for 99% confidence from the Student's *t* table and taking the least sum square of the products. An average of the uncertainties for each configuration was taken so as to find one uncertainty indicative of the configuration.

The axial bed temperatures for all trials did show some overall trends. The temperatures through the catalyst bed tended to show higher temperatures near the entrance than at the exit. In fact, some of the runs produced a temperature spike near the entrance, which was shown in the axial average bed temperature plot (figure 32). After the initial spike, the temperature typically decreased to just before the exit in an inverse exponential fashion. At the exit, each of the trials showed a sharp drop in bed temperature. Also, as indicated by table 3, each of the independent variables increased overall bed temperature in their high setting in comparison to their low settings although typically not much more than twice the uncertainty (figures 32 – 34).

Changes to bed temperatures through the catalyst bed were proportional to the air ratio. While the increase in the air ratio increased the overall average bed temperature by 13°C between its high and low settings of 0.672 and 0.608, most of the bed temperature difference occurred near the entrance of the bed (average of 25°C) and became less near the bed exit (average of 4°C).

The increase in the inlet temperature of 300°C to 400°C increased the overall temperature profile as well (figure 33). Although the inlet temperature had a greater effect on the overall temperature (average of 17°C increase) than that for the air ratio, the temperature difference between the settings was much higher near the entrance (average of 73°C). The temperature difference quickly decreased through the thermal spike and on through the bed until the bed exit temperature was actually lower for the higher inlet temperature setting. It is also interesting to note that the high and low settings for both the air ratio and the inlet temperature exhibited similar profiles, and that the overall

average bed temperature for the high and low settings of both variables were very similar (within 2°C for each level).

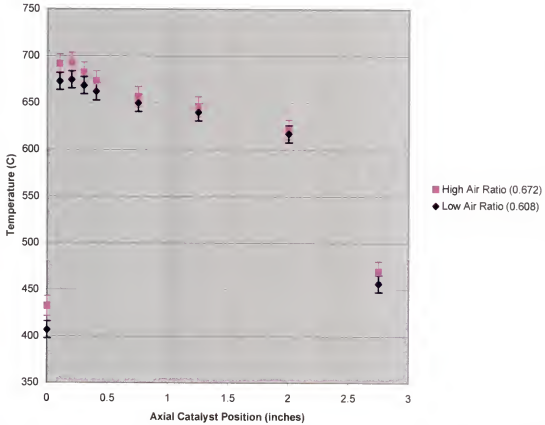


Figure 32: The effect of the air ratio on catalyst bed temperature

An increase in space velocity from 20,000 to 25,000 GHSV also increased bed temperatures (7°C), but less than either the air ratio or the inlet temperature. The effects of space velocity were more pronounced near the exit of the bed with an average temperature increase of nearly 33°C (figure 34). Although the bed exit accounted for a substantial portion of the overall average bed temperature difference, the temperatures at the beginning of the bed also experienced an increase (7-8°C) between the two space velocity settings. While the temperature at the entrance and exit of the bed increased with space velocity, the middle of the bed was nearly identical in temperature at both

settings. The axial location of the maximum temperature did not change with the space velocity although a larger region of high temperatures did exist at the higher space velocity setting.

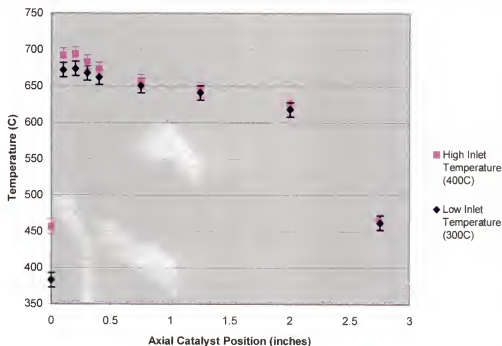


Figure 33: The effect of inlet temperature on catalyst bed temperature

Determination of the Effects and Interactions of the Independent Variables on Specific Efficiency and Conversion

While the overall average specific efficiencies and conversions achieved by the reformer were $22.64 \pm 2.06\%$ and $57.4 \pm 3.44\%$ respectively, the average specific efficiency increased with the high settings of all variables. The conversion did not follow the same trend.

In order to determine the effect of the independent parameters on the specific efficiency and conversion, effects and interactions were calculated and compared to signal to noise error at a 95% confidence interval for significance (see appendix D).

Although the effects of all variables were statistically significant for the specific efficiency, the space velocity was most significant in increasing the specific efficiency followed by the inlet temperature and the air ratio (table 4). The interactions between air ratio and space velocity and between inlet temperature and space velocity were significant as well for the specific efficiency (see appendix F for raw data).

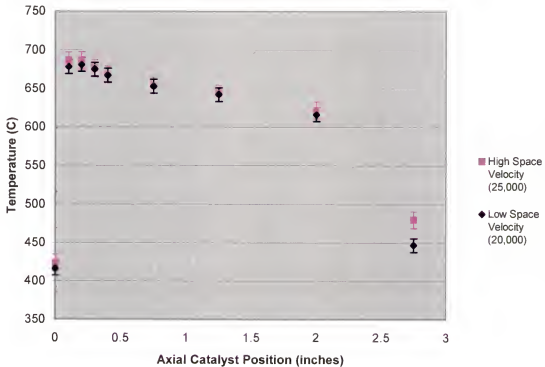


Figure 34: Effect of space velocity on the catalyst bed temperatures

Besides the effect of the space velocity itself, the interaction between the inlet temperature and the space velocity was the most significant specific efficiency within the ranges tested. Although changes in the inlet temperature were significant to the possible effect of space velocity on specific efficiency (average increase of 8.62%), the resultant magnitude of the interaction was not the sum, but approximately the average of the individual effects of the space velocity and inlet temperature. Also, the majority of the

contribution to the interaction arose by changing the inlet temperatures at high space velocities (90% of the interaction). The interaction between the air ratio and the space velocity was also found to be significant to the specific efficiency. Similar to the interaction between the space velocity and inlet temperature, the effect of the air ratio on specific efficiency was greater at the high as opposed to low space velocity setting.

The trend was approximately opposite for conversion. Any increases within the experimental range of the independent variables from their low to high settings resulted in reductions in the conversion. The interaction between the inlet temperature and the space velocity provided the most significant affect on the conversion although the effects of inlet temperature and space velocity themselves were significant. As for the specific efficiency, the change in inlet temperature at increased space velocity was the greatest contributor to the interaction for conversion (approximately 93%). The table below lists the change in the dependent variables for a change in the settings of each of the effects as well as interactions of the independent variables.

Table 4: Changes in specific efficiency and conversion with the effects and interactions the independent variables

Effects	Specific Efficiency	Conversion
Air Ratio	5.2	not significant
Inlet Temperature	6.9	-6.87
Space Velocity	10.6	-5.98
Interactions		
Air Ratio	not significant	not significant
Inlet Temperature		
Inlet Temperature	8.62	-7.91
Space Velocity		
Air Ratio	4.33	not significant
Space Velocity		
All Three	not significant	not significant

Discussion of results

The results of the experimentation provide several trends. In order to better understand these trends, the temperature of the bed was used as an indication of the speed and extent of the combustion, reforming and water-gas-shift reactions as well as the heat losses occurring within the bed. Although the bed temperature aided in correlating the experimental results with reaction chemistry, the exact rationale was not known from bed temperatures due to the unknown catalytic effect on the reaction.

Catalyst Bed Temperatures

Bed entrance temperature

It was found that the temperature at the entrance of the bed was higher for all independent variables at their high setting (figures 32 – 34). The thermocouple used to acquire this temperature was located just before the catalyst bed entrance. Thus, the increase in temperature was presumed to occur based on back radiation from the catalyst bed entrance since no other major sources of heat were available in the vicinity. Although assumed heated by radiation, the bed entrance temperature had less of a temperature difference than the 100°C difference dictated by the reformer inlet temperature settings. This was most likely due to the different rates of heating in the section between the inlet temperature thermocouple and the bed entrance thermocouple.

The temperature difference may also have been caused by pre-catalyst bed reforming reactions. A reformer does not require a catalyst to convert reactants to products. Since the overall autothermal reaction is endothermic, the heat provided by the reactant conditioning section may have been utilized for autothermal reforming before the catalyst bed, thus lowering the bed inlet temperature.

Combustion section bed temperatures

Typically a temperature spike occurred after entering the catalyst bed. Since the highest concentration of oxygen occurs at the entrance, the dramatic increase in temperature was the result of the combustion of fuel with the oxygen available (figures 32 – 34). This was proven by the resultant temperature increase in this section with an increase in the air ratio. The temperature increase with air ratio was not as great in magnitude as expected due to competing combustion and endothermic reforming reactions.

The inlet temperature had a similar effect (figure 33). Since an increased inlet temperature adds to the energy available at the entrance of the bed, the burden of bringing reactants to the reaction temperature was reduced. Thus the heat from the oxygen needed to combust the fuel that would be used for this purpose was used to increase combustion zone temperature. Unlike the inlet temperature and the air ratio, increases in the space velocity were not expected to add energy to the combustion zone. Thus only 5 to 8°C increases in bed temperatures near the temperature spike were observed with the increase in space velocity instead of the nearly 20°C temperature difference for both the air ratio and the inlet temperature. Thus the experimental combustion zone temperature difference with space velocity was attributed to enhanced mixing of the reactants and lower thermal losses between the entrance of the reformer and the entrance of the bed.

The remainder of the bed temperatures

The remainder of the catalyst bed reduced in temperature in an inverse exponential fashion until the exit (figures 32 – 34). The reforming and water gas shift reactions were assumed to dominate in this region of the catalyst bed since these reactions together are endothermic. In this case, it is assumed that the concentration of CO increases through

the bed from the endothermic reforming reaction, which lowers the temperature as the flow proceeds through the catalyst bed. With lower bed temperatures, the reforming reaction rate would decrease thus allowing the exothermic water gas shift reaction to dominate. This would then slow the decrease in the bed temperatures towards the exit producing the inverse exponential slope in axial bed temperature. The temperature drop could also be associated with heat loss to the environment although this effect was potentially insignificant due to the central location of the thermocouples and the insulation placed around the catalyst bed. The bed exit temperature departed from the inverse exponential type temperature decline though the bed with a sharp drop in temperature. This was presumably due to heat transfer losses since the final catalyst bed thermocouple was placed close to, but outside the exit of the bed.

While various temperature differences existed in the combustion section for many configurations, the temperatures near the exit of the bed for all trials were within 3°C of each other. This indicated that the effects of the independent variables on reactions occurring near the exit of the bed were less influential on bed temperature than in the combustion section (figures 32 – 34). The only significant change in axial bed temperatures occurred at the bed exit with a change in space velocity. Since it was experimentally found that the oxygen fraction was nearly zero in the reformer effluent, only a small fraction would have been available at the catalyst bed exit. Thus, the only method of temperature increase was from the heated flow upstream, which would carry more energy out of the bed at higher space velocities.

Specific Efficiency and Conversion

While the average theoretical specific efficiency was 34.5% calculated using constant temperature chemical equilibrium for the settings of the independent parameters, this assumed that nearly all fuel specie was reacted. By reducing the fuel fraction in the equilibrium calculation by the conversion, the average theoretical specific efficiency dropped to nearly zero thus promoting the combustion rather than the reforming reaction. Since the average experimental specific efficiency was not zero, global reaction equilibrium was not attained.

In order to provide better understanding of the independent variables on the reforming process, the bed temperatures were used as indications of the chemical reactions occurring within the catalyst bed. The temperature at the entrance of the bed was used to help determine the effects of the independent variables on specific efficiency and conversion since the average axial temperatures for the remainder of the bed were typically similar for each effect, which indicates similar reaction chemistry for all trials. From the assumed catalyst bed chemical reactions and the definition of the specific efficiency, increases in the specific efficiency arose from hydrogen and carbon monoxide produced from the endothermic reforming reaction and the energy contained in the effluent energy of the reactor. Since the exhaust energy contribution to the effects on specific efficiency were typically less than for the hydrogen and carbon monoxide energy, it was assumed that the specific efficiency was primarily driven by the ability for the catalyst to reform isooctane with a prescribed set of inlet conditions (figure 35).

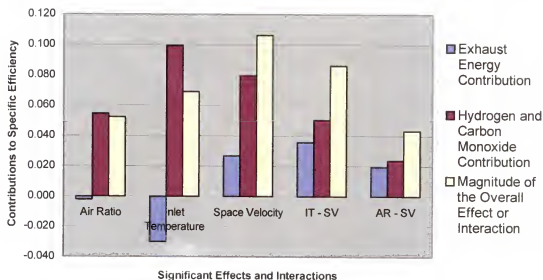


Figure 35: Contributions of exhaust energy and hydrogen and carbon monoxide energy to the specific efficiency

In order for the reforming reaction to occur favorably, high concentrations of reactants, the heat required for the reaction and residence time in the catalyst bed were necessary. The specific efficiency eliminates conversion from the efficiency calculation. Although the conversion was eliminated, the effect of residence time still exists in the specific efficiency through the non-equilibrium sub-reactions required for production of the desired hydrogen and carbon monoxide specie. Due to the number of potential products and complexity of possible reaction pathways to the desired hydrogen and carbon monoxide products, only the primary equilibrium products were analyzed.

Since these sub-reactions have similar requirements for the overall reaction, primary increases in the specific efficiency were assumed to be achieved through better dispersion and utilization of the heat produced by the combustion portion of the catalyst bed or a higher concentration of reactant specie near the catalytic surface. While specie concentration near the catalytic surface can be primarily based on the regime of the fluid

flow, heat to the catalyst site may occur either through the substrate by conduction or through the fluid using convection. Unfortunately the two thermal pathways could not be deciphered individually during the experiment.

The effect of the independent variables on specific efficiency

When the air ratio was increased, the specific efficiency increased. Also with an increase in the air ratio, the combustion zone temperatures were higher and distributed through a larger portion of the bed than with a lower air ratio. Thus the increase in catalyst bed temperature (more active catalyst sites) and volume may have increased the specific efficiency. An increase in the air ratio, also decreases the reactant concentration for reforming by adding more inert nitrogen. While the decrease in concentration of reactants necessary for reforming theoretically reduces the reaction rate, the increase the specific efficiency was assumed due to the extra heat generated from the added oxygen present.

The effect of the inlet temperature had a greater effect on the specific efficiency than the air ratio. Although the temperature difference at the entrance of the catalyst bed was greater for the inlet temperature settings than with the air ratio (72°C as opposed to 25°C respectively), the other bed temperatures for the high settings of both the air ratio and the inlet temperature were nearly identical as were the bed temperatures for the lower settings. Since the first thermocouple after the catalyst bed entrance was placed approximately a tenth of an inch from the entrance, this indicated that the temperature of the first tenth of an inch of catalyst bed depth was the critical difference between the two effects for specific efficiency.

The inlet temperature also changed the reactant density at the entrance to the catalyst bed that potentially lowered the concentration of reactants at the catalyst bed

walls. Since the overall effect of increased inlet temperature increased the specific efficiency, the possible decrease in reaction rate caused by the decrease in reactant concentration from the low to high inlet temperature setting had a smaller effect on the specific efficiency than the added heat. Also, the increase in inlet temperature caused a decrease in the exhaust temperature. Thus if exhaust temperatures were not considered, the inlet temperature would have the greatest effect on specific efficiency (figure 36). The reduction in catalyst bed exhaust temperature was assumed to result from increased endothermic reforming.

The space velocity was the most significant variable for specific efficiency. Since the bed temperature profile was similar for both space velocity settings, it may be assumed that increased space velocity increased the specific efficiency over its low setting by having a larger difference in the effluent energy than with the other effects (figure 35), a better dispersion of heat through the catalyst bed and potentially by increasing the concentration of reactant specie at catalyst sites. Since the conduction heat transfer coefficient through the catalyst bed substrate was assumed similar for every run, any heat or mass transfer differences were assumed to be primarily due to fluid flow through the bed.

It was unlikely that the specific efficiency may have changed due to better heat dispersion and increased mass transfer through the bed, since the convection and mass transfer coefficients corresponding to the catalyst bed entrance flow at both space velocities were the same (average $Re = 3.25$). This Reynolds number was calculated using the hydraulic diameter of a shaft of the honeycomb catalyst, and the density, viscosity and the velocity of the reactants at the catalyst bed entrance temperature.

Although theoretically there was no influence of space velocity on the heat or mass transfer coefficient, the surface roughness of the catalyst bed walls may have tripped the local flow to turbulent resulting in heat and mass transfer terms, which then would be more sensitive to changes in space velocity. Additionally, the change in space velocity may have provided a better specie concentration at the catalyst wall by promoting better mixing through the perforated plates placed before the catalyst bed.

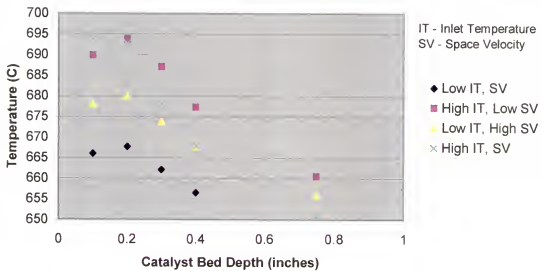


Figure 36: Catalyst bed entrance temperatures for interactions between inlet temperature and space velocity

The interaction between space velocity and inlet temperature was a significant interaction as well for the specific efficiency. The experimental data for the interaction indicated that the change in inlet temperature at higher space velocities was the primary contributor to the interaction (figure 36). Upon analyzing the catalyst bed temperatures, increasing the space velocity increased the maximum catalyst bed temperature and moved its location nearer to the entrance of the catalyst bed where reactant concentrations were highest as compared to the low space velocity. This indicated either

better mixing of the reactants before the bed or imposed turbulence within the channels.

The same effect on bed temperature was observed for the interaction between the air ratio and the space velocity (figure 37).

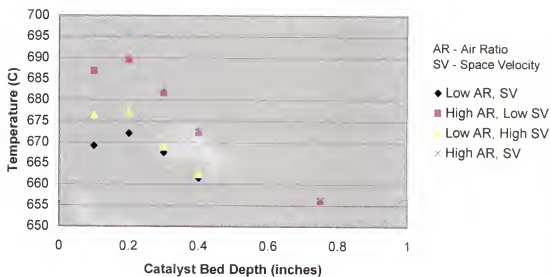


Figure 37: Catalyst bed entrance temperatures for interactions between air ratio and space velocity

The effect of the independent variables on the conversion

While specific efficiency increased with each of the independent variables, the opposite occurred for the conversion. Like specific efficiency, conversion as well can be theoretically connected to reaction kinetics, which is primarily driven by increased temperature, and increased reactant concentration at the catalyst (equations 18 and 19). Therefore a large fraction of the conversion most likely occurred at the entrance of the catalyst bed since it was the location of the highest reactant concentration and temperature although fuel conversion was also presumed to occur at lower rates in the remainder of the catalyst bed. Since conversion continued through the catalyst bed, the space velocity was also linked with conversion and thus can be a limiting factor.

Since nearly all of the temperature profiles were similar after the combustion region in the catalyst bed, any changes in the conversion most likely came from the conditions at the entrance to the catalyst bed. In fact, since the high settings of all the independent variables increased the temperature or the flow rate at the entrance of the catalyst bed, it can be assumed that the decrease in residence time in this critical area of the bed was decisive in lowering the conversion. Although the air ratio had an effect on the combustion zone catalyst bed temperatures, the difference in bed temperatures especially at the bed entrance temperature did not change significantly, thus air ratio had an insignificant affect on conversion. Increased space velocity reduced the residence time at the entrance of the bed by $\frac{1}{4}$ producing its affect on conversion. Increased inlet temperatures were also presumed to lower density by approximately $\frac{1}{4}$ at the entrance of the catalyst bed, which would have reduced reactant concentrations at the catalyst sites and lowered the local residence time making conversion more difficult. Thus the change in inlet temperature had more affect than the space velocity.

While the effects of space velocity and inlet temperature were significant, the decrease in conversion with their interaction was the most significant. The effect of the inlet temperature on conversion at high space velocities produced most of this interaction. Thus the space velocity acted to magnify the affect of the inlet temperature by further reducing the amount of time for conversion to occur.

CHAPTER 5 DISCUSSION

There are several issues that evolve from the results of this experimentation. Even though it was found from the experiment that increases in the all three independent parameters increased the bed temperatures as well as the specific efficiency of the reformer, conversion suffered a simultaneous loss. This result was presumed to be primarily driven by the reactant concentrations near the catalytic wall and catalyst bed temperature at the entrance of the bed. Thus precise control of the inlet temperature, air ratio and space velocity will be necessary for repeatable utility of an autothermal reformer. This may prove to be difficult if reactant vaporization must be completed for transients and may reduce the efficiency of the reformer greater than the 17.7% calculated.

The bed temperatures evolved within the catalyst bed also provided some insight to the reforming process although several potential problems arose during operation. While in operation and during start-up, the catalyst bed had great temperature differences due to the reactions occurring within the bed. The ceramic monolith used for a catalyst substrate experienced sometimes 300 to 400°C changes in temperature within 1 inch of catalyst bed depth during start-up and operation. These large temperature fluctuations in a monolithic substrate may generate significant stresses in the material and cause internal fractures depending on the method of stabilizing the catalyst bed for use and the method of cooling down the catalyst bed. If the thermal stresses become significant, increased start-up and shutdown time may be required for longevity making the bed less conducive

to automotive applications. Also, with such large temperature differences within the catalyst bed, proper thermal monitoring becomes an issue. While it may be assumed based on this research that the highest temperature in the catalyst bed will appear at the entrance, the exact location radially depends on the mixing occurring before the catalyst bed entrance. Further, unlike the inlet temperature or space velocity, varying the air ratio quickly heats the catalyst bed by introducing the oxygen necessary for combustion. So while the temperatures evolved in the bed were less than the maximum 900°C rating during testing, it was foreseen from the temperature sensitivity with air ratio that sintering may be an issue without proper control.

Control of the reactants was critical as well for the specific efficiency. While the total hydrogen fraction varied by 10% for the configurations chosen, the contribution of carbon monoxide in the effluent was small (1.5 to 4% of the total hydrogen fraction produced or less than 1% total). These levels of carbon monoxide reduce the necessity for a low temperature shift bed for PEM fuel cell use. While low, the fraction increased with all independent variables indicating that higher fractions were possible at optimal conditions. Since varying the inlet conditions can alter the carbon monoxide fraction, a less than optimal operating condition may be chosen for a reduction in plant size. Choosing a carbon monoxide reducing plant, which is less robust may be a critical issue with regards to operational reliability with the highly sensitive fuel cell.

The lack of complete conversion was also a critical issue. Unreacted fuel potentially damages the fuel cell stack and translates to losses in overall power plant efficiency. The results for this catalyst indicated that decreases in each of the independent variables increase conversion. Therefore operation of the reformer in the

design space covered by this experiment should be avoided. This was unfortunate since complete conversion at increased space velocities allows for reduced reformer volume. Since the interaction between inlet temperature and space velocity was the only significant variable calculated for conversion, manipulation of this interaction might yield better results.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

A 30 kilowatt autothermal reforming test rig was designed, built, instrumented and successfully operated for the purpose of experimentally studying the effects of several variables on the reforming process. The design of the rig involved creation of several novel parts such as the water vaporizer and superheater, the gas sampling system, the data acquisition program and the reformer itself. These parts as well as others added to the flexibility and utility of the rig. For this experiment, the rig was configured to show the effects and interactions of the air ratio, the space velocity and the inlet temperature on the bed temperature, efficiency and conversion.

There are several effective design considerations for enhancing the autothermal reforming of isooctane. It was found that the bed temperature did not change significantly beyond the first $\frac{1}{2}$ inch of catalyst bed depth for all trials. Thus, reactions occurring in the first 20% of the bed were responsible for the changes in the dependent variables. The greatest changes in this region occurred with inlet temperature and the air ratio.

It was found that although the effects of the inlet temperature and the air ratio were similar on the bed temperatures, the effect of inlet temperature on specific efficiency was greater than that of the air ratio. Since the only change in bed temperature between the air ratio and the inlet temperature occurred at the entrance of the bed, this was considered the area of highest activity for the specific efficiency.

While space velocity was the most significant factor for the specific efficiency, the inlet temperature was actually more significant in terms of the hydrogen and carbon monoxide produced. The interaction between the space velocity and the inlet temperature was found to increase the specific efficiency by an average of 8.9% of which 90% results from change in the inlet temperature at high space velocities. This indicates that inlet temperature was a significant variable for determining the possible space velocity for a given specific efficiency.

It was found that the conversion was decreased by each independent parameter and their interactions within the range tested. It was assumed that this was due to the decrease in density and residence time at the entrance of the catalyst bed for each of the independent parameters. The most negative affect on the conversion was the interaction between space velocity and inlet temperature (-7.91%). Since 93% of the interaction was found with a change in inlet temperatures at high space velocities, the decrease in conversion was presumed to be due to the magnification space velocity had on the difference in density and residence time indicated by the catalyst bed inlet temperature. Thus while increasing inlet temperatures resulted in higher specific efficiencies due to increased heat at the entrance of the bed, it also lowered reactant density and increased space velocity at the entrance of the bed reducing conversion.

Overall, greater mass transfer of reactants and higher heat transfer at the entrance of the bed may increase the specific efficiency and conversion of the reformer. There are several methods of increasing the heat transfer through the bed for larger active area and increasing concentration of the reactants. A mixing scheme in the bed or before the bed could be imposed to distribute hot gases in the bed and increase the concentration of

reactants at the catalyst bed walls. Although increased reformer pressure would also raise the reactant concentration near the catalyst surface, this method should not be used since it since there will also be a proportional to increase in the density of the flow bypassing the catalyst, which increases the amount of unconverted fuel.

The roughness of the catalyst or the substrate surface may be increased to trip the local Reynolds number in the boundary layer of the flow along the catalyst bed wall to the turbulent regime. This may increase the reactant concentration at the catalyst and provide better heat transfer to the rest of the catalyst bed. Heat also may be distributed to a larger portion of the bed by using a more conductive substrate with a catalyst more active at lower temperatures. Having a catalyst with a higher activity at lower temperatures would also decrease the amount of combustion necessary to convert the fuel resulting in increases in specific efficiency and conversion. Finally, since the bed inlet was the most critical location to reforming, the bed should be oriented such that this area is maximized. Enlarging the diameter of the catalyst bed may complete this and consequently provide for an optimal reformer volume.

There are many further studies, which would lead to a better understanding of the process. While varying the space velocity of the reformer within the 20,000 to 25,000 range was insightful, in order to fulfill the transients and flow ranges that may be required for automotive applications, better fuel and water vaporization techniques should be used. Some experimentation has been completed on micro-channel vaporizers, which could find application in the area of reactant vaporization. An additional option for fuel vaporization is direct injection. A study of the effects of various types of direct injection of various fuels may have potential to increase the overall rig efficiency by using the

existing product heat from the combustion reaction to vaporize the fuel and water. Also, transients in power systems tend to produce undesirable products, thus a study of the processes during expected transients of an automobile application would be useful to determine potential problems with operating an autothermal reformer in this mode.

Although the air ratio was theoretically more significant than the steam to carbon ratio for the efficiency (figures 11 and 12), increasing the S/C ratio can significantly lower combustion temperatures. Thus decreasing the S/C ratio below the experimental value of 3.0 may improve the specific efficiency by allowing for lower air ratios at similar bed temperatures. An experimental verification of this hypothesis could help to optimize the fuel processor performance.

It is important to note that the results presented do not take into account catalyst type, substrate nor geometry. While it may be assumed that greater precious metal content and greater surface area catalyst substrates will increase the benefits of using the catalyst, these conjectures have yet to be fully proven experimentally for an autothermal reformer. Thus further study on the influence of catalyst chemistry, the effects of surface area and bed geometry would be beneficial to the field.

The definition of specific efficiency is particular to fuel cells and is primarily based on the first law of thermodynamics. A second law analysis may be completed on the reformer by taking into account entropy change to the environment and to the fluid, which may yield interesting findings for future work.

Carbon formation from a steam reforming perspective is a relatively well known phenomenon. Unfortunately relatively little has been published for autothermal reformers. Due to the energy intensity of water vaporization, reduction of the water

necessary for autothermal reforming without carbon formation would yield higher overall reformer efficiencies (η_{ES}) and increase the reformers ability to complete transients (figure 15). Thus further study on the working limits for reactant concentrations for carbon formation and discovery of other possible carbon limiting catalyst chemicals for autothermal reformers would be of interest. Also, carbon particles are formed in various sizes thus a study of the degradation processes for various sized carbon particles should be studied for various substrates and catalysts.

Since gasoline is not the only fuel that can be used for hydrogen production on vehicles, various fuels should also be studied for their reforming characteristics and catalyst life under both autothermal and partial oxidation fuel processing methods. Since most transportation fuels do not purely consist of only one chemical, catalyst degradation studies may be completed for various fouling and poisoning agents that may exist in fuels as well.

From a fuel processing sub-system perspective, the mass of the reformer should be minimized for faster start-up and transient response as well as size considerations. Thus a study of the materials and structure of the reformer would aid in the reduction of heat loss and time needed to perform transients. Further, a study of fuel processor systems design may allow for increases in efficiency by combining several parts of the fuel processor.

The equation for the efficiency (η_{ES}) was formed under the assumption that none of the thermal energy available in the products was applied to the conditioning of the reactants. If the reformer products could supply all the heat necessary for the reactant conditioning, efficiency gains of 20% are possible (inlet temperature of 700K and steam

to carbon ratio of 3). Thus study of heat transfer methods and materials for reformat would be of interest.

When the air ratio of an autothermal reformer is reduced to zero, the reformer is typically considered a steam reformer. In this mode of operation, the reformer has the maximum theoretical efficiency since heat required for the reforming reaction is not typically included in the efficiency. In this scenario, the heat typically provided by the combustion of the fuel in an autothermal reformer would then have to either come from conduction of combustion heat through the walls of the reformer as a typical steam reformer or from conduction into the reactants to raise the inlet temperature. A study of increasing the inlet temperature until a steam reforming reaction can be completed would be interesting from the perspective of whether a fuel cell power plant has enough excess energy to complete this for conventional fuels such as gasoline and if this process would be any more efficient than current autothermal designs.

APPENDIX A COMPUTER PROGRAM

A program based on the graphical user interface LabView was created to acquire data and control various heaters throughout the rig. Included is the front panel, as well as the basic block diagram logic behind the program. The front panel gives access to several key vaporizer and superheater temperature readings and controls. The axial bed temperature and location are provided as well. Although automatic reactant control is possible, for safety considerations, manual control was implemented. Finally, several input variables were shown on the front panel so as to allow the user to calculate experimental set points while running the rig without changing the experiment. The lower right hand corner was dedicated to file storage control (figure 38).

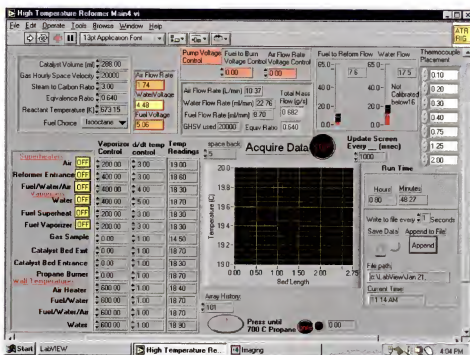


Figure 38: Front panel of program

Once the set points were calculated, the recommended pump voltages were calculated using calibrations and displayed on the front panel. In this step, another subVi was used to acquire heater and fluid temperatures throughout the rig. These temperatures were displayed on the front panel, placed into an array, which allowed a d/dt to be calculated in order to enhance heater control (figure 40).

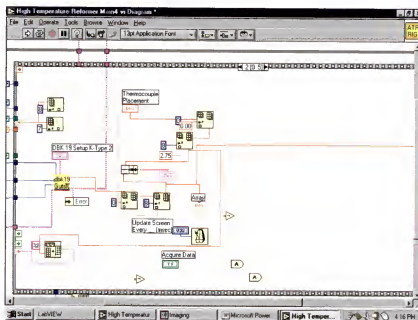


Figure 41: Computer timing and additional temperature acquisition

Additional temperature acquisition was necessary for the catalyst bed. The temperatures were again set into an array, which was output to the graph on the front panel. Timing of the data acquisition as well as tabulation of thermocouple axial set points were completed during this step of programming as well (figure 41).

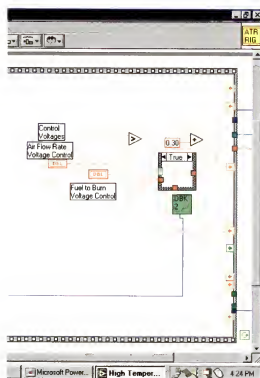


Figure 43: Analog control of the air flow and fuel

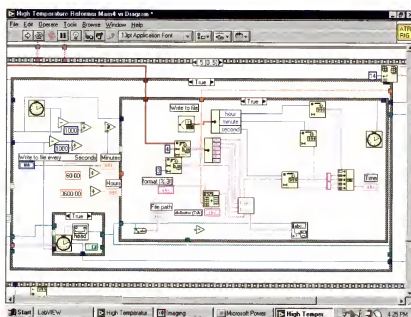


Figure 44: File Storage

The final portion of the program collected the temperature readings from the rig and experimental set points, formatted an output file and wrote the data to the file. This file was then imported to Excel for further calculations. This final step was skipped if the save data button was on engaged (figure 44).

APPENDIX B CALCULATION OF EFFICIENCY AND CONVERSION

Equations for Efficiency and Conversion Based on Acquired Data

The definition used for specific efficiency was

$$\eta_{sp} = \frac{Energy_{H_2} + Energy_{CO} + Energy_{Exhaust}}{Energy_{fuel in}} \bigg/ Conversion \quad (30)$$

where

$$Energy_{H_2} = \frac{H_2 \cdot flowrate_{Dry Sample} \cdot t \cdot \rho_{H_2} \cdot m_{in} \cdot LHV_{H_2}}{m_{Sample} \cdot MW_{H_2}} \quad (31)$$

and

$$Energy_{CO} = \frac{CO \cdot flowrate_{Dry Sample} \cdot t \cdot \rho_{CO} \cdot m_{in} \cdot LHV_{CO}}{m_{Sample} \cdot MW_{CO}} \quad (32)$$

In this equation, t was the time in minutes of the trial, $\rho_{Dry Sample}$ was the density of the sample after passing the water trap, m_{in} was the total mass into the reformer, $m_{Sample Out}$ was the total mass of the sample taken and H_2 and CO were the fractions of hydrogen and carbon monoxide in the sample stream after the water separator. The $\rho_{Dry Sample}$ was found by substituting the pressure, temperature and average molecular weight at the sample flow meter into the ideal gas equation.

$$m_{Dry\ Sample} = \left(\frac{(CO \cdot \rho_{CO}) + (CO_2 \cdot \rho_{CO_2}) + (H_2 \cdot \rho_{H_2}) + (N_2 \cdot \rho_{N_2}) + (H_2O \cdot \rho_{H_2O(g)}) + (C_8H_{18} \cdot \rho_{C_8H_{18}(g)})}{(H_2 \cdot \rho_{H_2}) + (N_2 \cdot \rho_{N_2}) + (H_2O \cdot \rho_{H_2O(g)}) + (C_8H_{18} \cdot \rho_{C_8H_{18}(g)})} \right) \cdot t \cdot flowrate_{Dry\ Sample} \quad (33)$$

where the densities were found using sample temperatures and pressures. For example

$$\rho_{CO} = \frac{P_{Sample} \cdot MW_{CO}}{R \cdot T_{Sample}} \quad (34)$$

While fractions for CO, CO₂ and H₂ were found using gas analyzers, isooctane and water fractions were found using the vapor pressure of the specie at the water trap temperature and pressure. For example, the water fraction was found using

$$H_2O = \frac{V_p(T_{Trap})}{P_{amb} - P_{Losses}} \quad (35)$$

where P_{Losses} is a set tubing loss from the reformer to the trap. Since all other specie were found, the nitrogen was assumed to make up the rest of the flow. The dry sample flow rate (flowrate_{Dry Sample}) was then found by visual inspection of its rotameter and dividing the corresponding air flow by a correction factor based on the temperature, pressure and density.

$$CF = \frac{MW_{ave} \cdot T_{Sample} (Rankine) \cdot 14.7}{MW_{air} \cdot 530 \cdot P_{Sample} (psia)} \quad (36)$$

where

$$MW_{ave} = \left(\frac{(MW_{CO} \cdot CO) + (MW_{CO_2} \cdot CO_2) + (MW_{H_2} \cdot H_2) + (MW_{N_2} \cdot N_2) + (MW_{H_2O} \cdot H_2O) + (MW_{C_8H_{18}} \cdot C_8H_{18})}{(H_2 \cdot \rho_{H_2}) + (N_2 \cdot \rho_{N_2}) + (H_2O \cdot \rho_{H_2O(g)}) + (C_8H_{18} \cdot \rho_{C_8H_{18}(g)})} \right) \quad (37)$$

The total mass in (m_m) was found by multiplying the mass flow rates of the reactants by the time of the run.

$$m_m = \left(\dot{V}_{C_8H_{18}} \cdot \rho_{C_8H_{18}(l)} + \dot{V}_{H_2O} \cdot \rho_{H_2O(l)} + \left(\dot{V}_{Air} \left(\frac{P_{amb} \cdot MW_{Air}}{R \cdot T_{amb}} \right) \right) \right) \cdot t \quad (38)$$

The total mass of the sample (m_{Sample}) was found by multiplying the dry sample flow rate with density and adding in the mass of the trapped specie (V_T).

$$m_{Sample} = m_{Dry\ Sample} + \rho_{H_2O} \cdot V_{T_{H_2O}} + \rho_{C_8H_{18}} \cdot V_{T_{C_8H_{18}}} \quad (39)$$

The energy input to the reformer was assumed to only come from the fuel. Thus

$$Energy_m = \dot{V}_{C_8H_{18}} \cdot \rho_{C_8H_{18}(l)} \cdot t \cdot \frac{LHV_{C_8H_{18}}}{MW_{C_8H_{18}}} \quad (40)$$

Further, the fuel conversion was defined as

$$Conversion = 1 - \frac{fuel\ out}{fuel\ in} \quad (41)$$

$$Conversion = 1 - \frac{(flowrate_{Dry\ Sample} \cdot t \cdot C_8H_{18} \cdot \rho_{C_8H_{18}(g)} + \rho_{C_8H_{18}(l)} \cdot V_{T_{C_8H_{18}}})}{\dot{V}_{C_8H_{18}} \cdot \rho_{C_8H_{18}(l)} \cdot t} \quad (42)$$

In order to calculate the exhaust energy for the specific efficiency equation, the mass fractions of the sampled specie were needed.

$$CO_{mass} = \frac{CO \cdot flowrate_{Dry\ Sample} \cdot t \cdot \rho_{CO}}{m_{Sample}} \quad (43)$$

$$CO_{2\ mass} = \frac{CO_2 \cdot flowrate_{Dry\ Sample} \cdot t \cdot \rho_{CO_2}}{m_{Sample}} \quad (44)$$

$$H_2O_{mass} = \frac{H_2O \cdot flowrate_{Dry\ Sample} \cdot t \cdot \rho_{H_2O} + \rho_{H_2O} \cdot V_{T_{H_2O}}}{m_{Sample}} \quad (45)$$

$$C_8H_{18, \text{mass}} = \frac{C_8H_{18} \cdot \text{flowrate}_{\text{Dry Sample}} \cdot t \cdot \rho_{C_8H_{18}} + \rho_{C_8H_{18}} \cdot V_{I_{C_8H_{18}}}}{m_{\text{Sample}}} \quad (46)$$

$$H_{2, \text{mass}} = \frac{H_2 \cdot \text{flowrate}_{\text{Dry Sample}} \cdot t \cdot \rho_{H_2}}{m_{\text{Sample}}} \quad (47)$$

$$N_{2, \text{mass}} = \frac{N_2 \cdot \text{flowrate}_{\text{Dry Sample}} \cdot t \cdot \rho_{N_2}}{m_{\text{Sample}}} \quad (48)$$

Therefore the exhaust energy was calculated by

$$\text{Energy}_{\text{Exhaust}} = \left[\begin{aligned} & \left((CO_{\text{mass}} / MW_{CO}) \cdot \Delta h_{CO} + (CO_{2, \text{mass}} / MW_{CO_2}) \cdot \Delta h_{CO_2} \right) \\ & + (H_2O_{\text{mass}} / MW_{H_2O}) \cdot \Delta h_{H_2O} \\ & + (C_8H_{18, \text{mass}} / MW_{C_8H_{18}}) \cdot \Delta h_{C_8H_{18}} \\ & + (H_{2, \text{mass}} / MW_{H_2}) \cdot \Delta h_{H_2} + (N_{2, \text{mass}} / MW_{N_2}) \cdot \Delta h_{N_2} \end{aligned} \right] \cdot m_{\text{ex}} \quad (49)$$

where the change in enthalpy was found by integrating the specific heat. For example

$$\Delta h_{H_2O} = \int_{T_{in}}^{T_{out}} C_{p_{H_2O}}(T) dt \quad (50)$$

Although the specific efficiency equation was a calculation for only the converted fuel, isooctane was included for the exhaust energy calculation since thermal energy was required to increase the temperature of the unconverted fuel as well as the rest of the products.

Sample Calculation

A sample calculation was performed using experimental data from the low space velocity, low air ratio and low inlet temperature configuration.

$$\dot{V}_{C_8H_{18}} = 10.35 \text{ ml/min}, \dot{V}_{H_2O} = 27.06 \text{ ml/min}, \dot{V}_{\text{Air}} = 11.71 \text{ L/min}$$

$$V_{TH_2O} = 380 \text{ ml}, V_{IC_8H_{18}} = 20 \text{ ml}, \text{Sample flowrate} = 15933.4 \text{ ml/min}$$

$$T_{Sample} = 297.6K, T_{Trap} = 280.1K, T_{amb} = 300.1K, T_{out} = 799.1K, T_{in} = 574.4K,$$

$$P_{Sample} = 7.93psia, P_{amb} = 101.350kPa, P_{losses} = 26.7kPa$$

$$H_2 = 0.159, CO_2 = 0.146, CO = 0.0034, t = 20.58min$$

Since the vapor pressures of water and isooctane at T_{Trap} were 1.03 and 2.6 kPa respectively, the fractions of water and isooctane were calculated using equation 35. For this calculation, the pressure losses were necessary to find pressure at the trap.

$$H_2O = \frac{1.03kPa}{74.63kPa} = 0.0138$$

$$C_8H_{18} = \frac{2.6kPa}{74.63kPa} = 0.0348$$

Using these fractions, the fraction of nitrogen was found.

$$N_2 = 1 - 0.0138 + 0.0348 + 0.159 + 0.146 + 0.0034 = 0.643$$

The densities of the specie were then found using equation 34.

$$\rho_{co} = \frac{54660Pa \cdot 28 \frac{g}{mol}}{8.314 \frac{J}{mol \cdot K} \cdot 297.65K \cdot 1000000 \frac{ml}{m^3}} = 0.00115 \frac{g}{ml}$$

Similarly the densities for carbon dioxide, hydrogen, nitrogen, isooctane, and water were 0.0018, 0.0000818, 0.00115, 0.00466, and 0.00074 g/ml respectively.

The average molecular weight was then found using equation 37.

$$MW_{ave} = \left(\frac{(28 \cdot 0.0034) + (44 \cdot 0.146) + (2 \cdot 0.159)}{(28 \cdot 0.643) + (18 \cdot 0.0138) + (114 \cdot 0.0348)} \right) = 29.05 \frac{g}{mol}$$

The correction factor was then calculated using equation 36.

$$CF = \frac{\frac{29.05 \frac{g}{mol}}{28.8 \frac{g}{mol}} \cdot 297.6 K \cdot 1.8(\text{for Rankine}) \cdot 14.7 \text{ psia}}{530^\circ R \cdot 7.93 \text{ psia}} = 1.488$$

This allowed for calculation of the sample flow rate.

$$\text{flowrate}_{\text{Dry Sample}} = \frac{15933.4 \frac{ml}{min}}{1.488} = 10707.1 \frac{ml}{min}$$

The mass into the reformer was calculated using equation 38 to be

$$m_{in} = \left(\left(10.35 \frac{ml}{min} \cdot 0.69 \frac{g}{ml} + 27.06 \frac{ml}{min} \cdot 1 \frac{g}{ml} + \right. \right. \\ \left. \left. 11710 \frac{ml}{min} \left(\frac{101350 Pa \cdot 28.8 \frac{g}{mol}}{8.314 \frac{J}{mol \cdot K} \cdot 300.1 K \cdot 1000000 \frac{ml}{m^3}} \right) \right) \right) \cdot 20.583 \text{ min} \\ = 986 g$$

The dry sampled mass was calculated using equation 33 as

$$m_{\text{Dry Sample}} = \left(\left(0.0034 \cdot 0.000528 \frac{g}{ml} \right) + \right. \\ \left(0.146 \cdot 0.00083 \frac{g}{ml} \right) + \\ \left(0.1592 \cdot 0.0000377 \frac{g}{ml} \right) + \\ \left(0.643 \cdot 0.000528 \frac{g}{ml} \right) + \\ \left(0.0138 \cdot 0.000339 \frac{g}{ml} \right) + \\ \left(0.0348 \cdot 0.00215 \frac{g}{ml} \right) \right) \cdot 20.583 \text{ min} \cdot 10707.1 \frac{ml}{min} \\ = 120.74 g$$

The total sampled mass was calculated using equation 39 as

$$m_{\text{Sample}} = 120.74 \text{ g} + 1 \frac{\text{g}}{\text{ml}} \cdot 380 \text{ ml} + 0.69 \frac{\text{g}}{\text{ml}} \cdot 20 \text{ ml} = 514.54 \text{ g}.$$

The energy for hydrogen and carbon monoxide output was then found through equations 31 and 32 respectively.

$$\text{Energy}_{\text{CO}} = \frac{\left(0.0034 \cdot 10707.1 \frac{\text{ml}}{\text{min}} \cdot 20.583 \text{ min} \cdot 0.000528 \frac{\text{g}}{\text{ml}} \cdot 986 \text{ g} \cdot 110.541 \frac{\text{kJ}}{\text{mol}} \right)}{514.54 \text{ g} \cdot 28 \frac{\text{g}}{\text{mol}}} = 3 \text{ kJ}$$

$$\text{Energy}_{\text{H}_2} = \frac{\left(0.1592 \cdot 10707.1 \frac{\text{ml}}{\text{min}} \cdot 20.583 \text{ min} \cdot 0.0000377 \frac{\text{g}}{\text{ml}} \cdot 986 \text{ g} \cdot 241.826 \frac{\text{kJ}}{\text{mol}} \right)}{514.54 \text{ g} \cdot 2 \frac{\text{g}}{\text{mol}}} = 306.5 \text{ kJ}$$

Next, equation 40 was used to calculate the energy into the reformer.

$$\text{Energy}_{\text{in}} = 10.35 \frac{\text{ml}}{\text{min}} \cdot 0.69 \frac{\text{g}}{\text{ml}} \cdot 20.583 \text{ min} \cdot \frac{5068.8 \frac{\text{kJ}}{\text{mol}}}{114 \frac{\text{g}}{\text{mol}}} = 6535.8$$

Then finally, the conversion was calculated using equation 41.

$$\begin{aligned} \text{Conversion} &= 1 - \frac{\left(10707.1 \frac{\text{ml}}{\text{min}} \cdot 20.583 \text{ min} \cdot 0.0348 \cdot 0.00215 \frac{\text{g}}{\text{ml}} \right.}{10.35 \frac{\text{ml}}{\text{min}} \cdot 0.69 \frac{\text{g}}{\text{ml}} \cdot 20.583 \text{ min}} \\ &\quad \left. + 0.69 \frac{\text{g}}{\text{ml}} \cdot 20 \text{ ml} \right) \\ &= 0.605 \text{ or } 60.5\% \end{aligned}$$

In order to find the energy contained in the exhaust, the mass fractions must be computed (equations 43 – 48).

$$CO_{\text{mass}} = \frac{0.0034 \cdot 10707.1 \frac{ml}{min} \cdot 20.583 min \cdot 0.000528 \frac{g}{ml}}{514.54g} = 0.000769$$

$$CO_{2\text{mass}} = \frac{0.146 \cdot 10707.1 \frac{ml}{min} \cdot 20.583 min \cdot 0.00083 \frac{g}{ml}}{514.54g} = 0.0519$$

$$H_2O_{\text{mass}} = \frac{\left(0.0138 \cdot 10707.1 \frac{ml}{min} \cdot 20.583 min \cdot 0.000339 \frac{g}{ml} + 1 \frac{g}{ml} \cdot 380ml \right)}{514.54g} = 0.74$$

$$C_RH_{\text{mass}} = \frac{\left(0.0348 \cdot 10707.1 \frac{ml}{min} \cdot 20.583 min \cdot 0.00215 \frac{g}{ml} + 0.69 \frac{g}{ml} \cdot 20ml \right)}{514.54g} = 0.0589$$

$$H_{2\text{mass}} = \frac{0.1592 \cdot 10707.1 \frac{ml}{min} \cdot 20.583 min \cdot 0.0000377 \frac{g}{ml}}{514.54g} = 0.00257$$

$$N_{2\text{mass}} = \frac{0.643 \cdot 10707.1 \frac{ml}{min} \cdot 20.583 min \cdot 0.000528 \frac{g}{ml}}{514.54g} = 0.145$$

Therefore the total exhaust energy was calculated (equation 49 and 50).

$$\begin{aligned}
 Energy_{exhaust} &= \left(\left(0.000769 \cdot 6.980 \frac{kJ}{mol} \right) \middle/ 28 \frac{g}{mol} \right. \\
 &\quad + \left(0.0519 \cdot 10.882 \frac{kJ}{mol} \right) \middle/ 44 \frac{g}{mol} \\
 &\quad + \left(0.74 \cdot 8.382 \frac{kJ}{mol} \right) \middle/ 18 \frac{g}{mol} \\
 &\quad + \left(0.0589 \cdot 45.896 \frac{kJ}{mol} \right) \middle/ 114 \frac{g}{mol} \\
 &\quad + \left(0.00257 \cdot 6.618 \frac{kJ}{mol} \right) \middle/ 2 \frac{g}{mol} \\
 &\quad \left. + \left(0.145 \cdot 6.813 \frac{kJ}{mol} \right) \middle/ 28 \frac{g}{mol} \right) \cdot 986g \\
 &= 437.91kJ
 \end{aligned}$$

making the specific efficiency through equation 30,

$$\eta_{sp} = \frac{306.5kJ + 3kJ + 437.91kJ}{6535.8kJ} \middle/ 0.492 = 0.189 \text{ or } 18.9\%.$$

APPENDIX C STATISTICAL DESIGN OF EXPERIMENTS

The statistical design on experiments is a method of experimentally covering a design space using the least number of trials, deciphering the effects and interactions of various variables and building an empirical model of the results. This appendix is a summary of the work assembled by Erickson.¹⁶

In order to accomplish this, each independent variable is tested at its corresponding high and low set points for a resultant dependent variable. Since testing of all combinations of variable states is necessary, the minimum number of trials can be calculated based on the number of independent variables (k).

$$\text{Trials}_{\min} = V^k \text{ where } V \text{ is the number of set points} \quad (51)$$

Thus if there are two variables and two set points for each variable, the minimum number of trials would be 4. Thus a matrix can be formed to help identify all trials by indicating +1 as the high set point and -1 as the low set point for a variable.

Table 5: Factorial matrix

Configuration	Independent Variable 1	Independent Variable 2	Dependent Variable
1	-1	-1	Y_{--}
2	+1	-1	Y_{+-}
3	-1	+1	Y_{-+}
4	+1	+1	Y_{++}

Once all runs have been delineated, the run order should be randomized to reduce error due to unforeseen variables. These variables may be a degradation in catalyst performance over time, or other such effects which promote process drift during experimentation. Also, to ensure statistical significance for each configuration, each run

should have at least two iterations bringing the trial total to 8. If a model of the experimental space is desired, a third iteration at the midpoint of each variable is necessary since the factorial design of experiments assumes a linear effect of each independent variable on the dependent variable. This may not be the case for all variables, thus testing is necessary.

It is assumed that the dependent variable for each configuration is the result of the effects of the set points of the independent variables. Thus the effect of a variable can be calculated by subtracting the average output variable when that variable is at its high set point from the average output variable when the variable is at its low set point. Interactions between variables can also be calculated by multiplying the map for the variable set points (i.e. $+1*-1 = -1$ and $-1*-1 = +1$) and using this product for the high and low set points (equations 28 and 29).

All variables will inevitably have some effect, or play some role in an interaction due to experimental errors and process drift although not all may be significant. The significance of these effects and interactions on the dependent variable can be found by comparing the uncertainty of the dependent variable with the noise band that can be expected for the number of trials. The calculation of the anticipated noise requires the pooled standard deviation, which is calculated using the sum of the variances from each configuration and the total degrees of freedom of the data set (equation 52).

$$S_p = \sqrt{\frac{\sum_{z=1}^r \sum_{k=1}^N (Y_k - \bar{Y}_z)^2}{V}} \quad (52)$$

where r is the number of configurations, N is the number of iterations in each configuration and V is the sum of the degrees of freedom for the data set.

Doubling the pooled standard deviation of the data and dividing by the square of the total number of trials typically calculates anticipated noise band, which is also known as the standard error (equation 53). In effect, this estimates the overall uncertainty in the data.

$$S_{L_e} = \frac{2 \cdot S_p}{\sqrt{n_F}} \quad (53)$$

The effect, or interaction is then divided by the standard error and compared to a critical signal to noise ratio for the degrees of freedom of the data set at a given confidence interval (equation 54).

$$t = \frac{E \text{ or } I}{S_{L_e}} \quad (54)$$

If the absolute value of the quotient of the effect, or interaction over the standard error (t) is larger than the critical signal-to-noise t ratio (t^* from Student's t table), then the effect or interaction can be considered significant.

An empirical model can be formed from the experimentation, which helps to predetermine performance of the system based on the independent variables. An equation of three independent variables for the dependent variable (Y) was shown for reference (equation 55). For the equation of the two independent variable system above, X_3 would be set to zero. Also, any insignificant effects (E), or interactions (I) would be set to zero.

$$Y = \bar{Y} + \frac{E_{R1}}{2} \times X_1 + \frac{E_{R2}}{2} \times X_2 + \frac{E_{R3}}{2} \times X_3 + \frac{I_{R12}}{2} \times X_1 \times X_2 + \frac{I_{R13}}{2} \times X_1 \times X_3 + \frac{I_{R23}}{2} \times X_2 \times X_3 + \frac{I_{R123}}{2} \times X_1 \times X_2 \times X_3 \quad (55)$$

Note that the actual values of X_1 , X_2 and X_3 are between -1 and $+1$. This range is proportional to the range between the high ($+1$) and low (-1) set points set up for each variable.

APPENDIX D SAMPLE CALCULATIONS BASED ON ACTUAL DATA

Table 6: Levels for the independent variables

	Low (-)	High (+)
A/F Ratio	0.608	0.672
Space velocity	20,000	25,000
Temperature	300°C	400°C

Table 7: Calculation of averages, variances and degrees of freedom from specific efficiency data

Config.	Air Ratio (AR)	Inlet Temperature (IT)	Space Velocity (SV)	Trial 1	Trial 2	Trial 3	Average (Y_{ave})	Variance	Degrees of Freedom
1	-	-	-	19.25	18.90	15.19	17.78	10.13	2
2	+	-	-	20.05	13.90	21.81	18.59	34.49	2
3	-	+	-	14.41	13.73	19.73	15.96	21.61	2
4	+	+	-	16.65	16.48	17.82	16.98	1.06	2
5	-	-	+	15.15	17.87	16.33	16.45	3.71	2
6	+	-	+	24.34	23.04	24.42	23.93	1.20	2
7	-	+	+	30.34	27.56	31.73	29.88	9.04	2
8	+	+	+	33.79	48.62	42.21	41.54	110.74	2

From this data, the pooled standard deviation, and the average of the data set was calculated (equation 52).

Table 8: Pooled Standard Deviation, Total Degrees of Freedom and the Average of the Averages for each Configuration

Pooled Standard Deviation	Total Degrees of Freedom for the Data Set	Average of Y_{ave}
3.46	16	22.6

Thus standard error was calculated as 0.023 using equation 53. The effects and interactions of the independent variables as well as the signal to noise ratios were then calculated for significance using equations 28, 29 and 54 (table 9).

Table 9: Calculated effects, interactions and signal-to-noise t-ratio

Configuration	AR	IT	SV	AR,IT	IT,SV	AR,SV	AR,IT,SV
1	-	-	-	+	+	+	-
2	+	-	-	-	-	+	+
3	-	+	-	-	+	-	+
4	+	+	-	+	-	-	-
5	-	-	+	+	-	-	+
6	+	-	+	+	+	-	-
7	-	+	+	-	-	+	-
8	+	+	+	+	+	+	+
Effects and Interactions	5.2	6.90	10.62	1.10	8.61	4.33	0.99
Signal-to-noise t-ratio	1.59	2.76	5.39	-1.34	3.97	0.94	-1.42

The critical signal-to-noise ratio at a 95% confidence interval and 16 degrees of freedom is 2.12. Therefore, since only the effects of the space velocity and the interactions of air ratio and space velocity and inlet temperature and space velocity have a signal-to-noise ratio greater than the critical value, the other effects and the interactions are left out of the empirical model (equation 55).

$$\eta_{sp} = \left(22.6 + \frac{5.2}{2} X_1 + \frac{6.9}{2} X_2 + \frac{10.62}{2} X_3 + \frac{8.61}{2} X_1 \cdot X_3 + \frac{4.33}{2} X_2 \cdot X_3 \right)$$

A similar process was used to find the empirical model for the conversion.

$$Conversion = \left(57.4 - \frac{6.87}{2} X_2 - \frac{5.98}{2} X_3 - \frac{7.90}{2} X_2 \cdot X_3 \right)$$

Additional examples can be found in Erickson and Lawson and Erjavec.^{16,42}

APPENDIX E ERROR CALCULATION

Equations Necessary to Calculate the Error

The error analysis was described for the equation $X = x_1 * x_m * x_n$, where N is the number of iterations and V is the number of variables. The error is separated into two distinct forms; resolution and precision. Resolution error typically arises from instruments while precision accounts for variances in the repeatability of a device.

Resolution Error

Since the dependant variable can be more sensitive to changes in different variables, the sensitivity index was calculated (equation 56).

$$\theta_i = \frac{\partial X}{\partial x_i} \quad (56)$$

For computation, all variables are set to their average values after taking the partial derivative.

The resolution error, or bias limit is an indication of the measuring abilities of the instrument used (equation 57).

$$R_i = 1/2 \text{ leastcount} \quad (57)$$

For example, if a ruler is the measuring instrument and has gradations at 1/8th of an inch, the least count is 1/8th of an inch. 1/2 appears in the equation since all measurements should be rounded to the nearest leastcount of the instrument.

The resolution limit, or bias error least sum squares all the possible errors with regard to the measuring instruments.

$$R_x = \sqrt{\sum_{i=1}^I (\theta_{x_i} R_{x_i})^2} \quad (58)$$

Precision Error

The standard deviation gives a measure of the precision of a measurement.

Summing the variances of each of the iterations of a given variable and dividing by the number of degrees of freedom for that variable calculates the standard deviation (equation 59).

$$P_x = \sqrt{\frac{\sum_{i=1}^N (x_{x_i} - \bar{x}_x)^2}{N-1}} \quad (59)$$

If the number of measurements are less than 25 measurements for a variable, the standard deviation of the means can be used in place of the standard deviation (equation 60).

$$P_{x_s} = \frac{P_{x_i}}{\sqrt{N}} \quad (60)$$

A total precision index can then be calculated for the sum of all the precision errors for each variable that make up the equation for the dependent variable in a method similar for the resolution limit (equation 61).

$$P_x = \sqrt{\sum_{i=1}^I (\theta_{x_i} P_{x_i})^2} \quad (61)$$

This is the amount the calculation will be off due to precision error.

The Welsh-Satterthwaite equation is then used to calculate the degrees of freedom for a multivariable system with various degrees of freedom for each variable. If every variable in the equation has the same degrees of freedom then the total degrees of

freedom for the equation is the same as the degrees of freedom for each variable (equation 62).

$$\nu = \frac{\left[\sum_{i=1}^r (\theta_{x_i} P_{x_i})^2 \right]}{\sum_{i=1}^r \frac{(\theta_{x_i} P_{x_i})^2}{(N-1)_{x_i}}} \quad (62)$$

Finally, the total uncertainty may be calculated using the resolution limit, precision index and a t value found using the Student's t table for the degrees of freedom and confidence interval required for the uncertainty (equation 63).

$$u_X = \sqrt{R_X^2 + (t_{\nu, 95\%} P_X)^2} \quad (63)$$

The Student's t table uses a normal distribution to provide a limit for the signal to noise ratio. Thus multiplying the student t table value by the precision error includes the potential noise in the reading of each variable.

While the equations above calculate error based on the independent variables in the equations for the dependent variable, the uncertainty may be calculated using another method. While the same procedure using the independent variables must be performed for the resolution error, the precision error portion of the uncertainty may be calculated from just the dependent variable. In this case, the pooled standard deviation is used in place of the precision error (equation 52). If the total number of measurements is less than 25, the pooled standard deviation of the means must be calculated which divides the pooled standard deviation by the square root of the total number of measurements. When using the pooled standard deviation, or pooled standard deviation of the means, the final calculation for the uncertainty uses the Student's t table value at the degrees of freedom of the data set rather than from the Welsh-Satterhwaite equation.

An uncertainty based on the iterations of a single configuration may also be calculated by using only values from each configuration. In this case, the degrees of freedom for the Student's *t* value is only of the configuration as well.

Sample Error Calculation

Due to the long and complicated equation formed when all equations for the specific efficiency and conversion were combined, each equation was taken separately for the resolution error. Thus the resolution error each equation used to find the conversion and specific efficiency was found through the sensitivity index. The partial derivatives of these equations, the subsequent plugging in of averages for the variables and taking the least sum squares of each of the equations were considered elementary and thus were not stated in this section. The averages used for the calculation can be found in the raw data section of the appendix.

Table 10: Leastcounts for various devices

Data Acquisition Device	Error
Gas Chromatograph %H ₂	1% of full scale
CO from analyzer	0.03% of full scale
CO ₂ from analyzer	0.6% of full scale
Water and Isooctane into reformer	±0.2 ml/min
Air into reformer	0.1 LPM
Flowmeter reading for sample	±2% of reading
Pressure	±0.2 psi.
Volume of fuel out	±1 ml.
Volume of water out	±2 ml.
Time of run	0.002 minutes
All Temperatures	±0.1K

The results of the calculations for the resolution error were errors of 0.0033 for the conversion and 0.0022 for the specific efficiency. The precision error for the data sets

were found by calculating the pooled standard deviation (degrees of freedom for the data set was 16 for both conversion and specific efficiency) and further dividing by the square root of the number of trials (24), which yielded errors of 0.0344 and 0.02 for the conversion and specific efficiency respectively.

APPENDIX F RAW DATA, PROCEEDURE AND MAJOR PARTS

Raw and Calculated Data

The data used for calculations is shown according to the configuration. The configuration code used relates to the state of the independent variables air ratio, inlet temperature and space velocity respectively.

Table 11: Raw Data

Configuration	V _{C₈H₁₈} (ml/min)	V _{water} (ml/min)	V _{air} (LPM)	Sample flowrate (air ml/min)	V _{TH₂O} (ml)	V _{TC₈H₁₈} (ml)	H ₂ (%)	CO (%)	CO ₂ (%)
-,-,-	10.35	27.06	11.71	15933.4	380	20	15.92	0.34	14.6
+,+,-	10.1	26.41	12.64	17105.5	347	6	13.21	0.36	14.3
-,+,-	10.35	27.06	11.71	16225.9	352	34	13.03	0.27	14.6
-,+,-	10.35	27.06	11.71	16518.8	390	9	11.03	0.17	14
+,+,-	10.1	26.41	12.64	17105.5	315	15	18.5	0.52	15.1
-,+,-	8.81	23.04	9.97	16812	365	12	21.72	0.51	15.3
-,+,+	12.93	33.82	14.64	17105.5	368	6	14.8	0.35	14.2
-,+,+	12.93	33.82	14.64	17105.46	332	4	18.23	0.47	15
-,+,+	8.81	23.04	9.97	17105.5	340	10	21.09	0.67	15.5
-,+,+	8.81	23.04	9.97	16518.8	380	10	22.76	0.41	14.9
-,+,+	12.93	33.82	14.64	17105.5	276	7	15.95	0.3	13.8
+,+,-	10.1	26.41	12.64	17693.26	306	1	21.08	0.66	15.1
+,+,-	8.6	22.49	10.76	17105.5	305	2	22.41	0.62	15.2
+,+,-	12.63	33.01	15.8	17399.2	301	9	21.54	0.64	15
-,+,+	11.01	28.8	12.47	16518.9	310	10	24.44	0.67	15.5
-,+,+	11.01	28.8	12.47	17693.26	300	10	25.4	0.77	15.4
+,+,-	8.6	22.49	10.76	17399.2	300	4	21.81	0.68	15.7
-,+,+	11.01	28.8	12.47	17105.5	330	30	24.6	0.72	15.6
+,+,-	12.63	33.01	15.8	17105.5	299	2	21.44	0.71	15.2
+,+,-	8.6	22.49	10.76	17399.2	310	5	23.31	0.72	15.7
+,+,-	12.63	33.01	15.8	17105.5	300	10	23.93	0.65	14.9
+,+,+	10.75	288.11	13.45	17693.3	270	4	28.38	1.08	15.5
+,+,+	10.75	288.11	13.45	17693.3	280	1	25.89	0.96	15.5
+,+,+	10.75	288.11	13.45	17693.3	240	1	24.51	0.98	15.5
Averages	10.648	60.343	12.68	17093.62	321	9.25	20.62	0.59	15

Table 11: Raw data continued

Configuration	T _{trap}	T _{sample} (K)	T _{in} (K)	T _{out} (K)	T _{amb} (K)	P _{sample} (mmHg)	t (min)
-,-,-	280	298	574.5	799.1	300	410	20.58
+,-,-	282.6	293.5	574.5	713.5	297	400	20.02
-,-,-	278.3	290.1	574.7	709.4	293	420	20
-,-,-	284.7	293.3	574	693.6	295	430	20.93
+,-,-	278.4	286.75	574.2	709	289	400	20.67
-,+,-	282.6	287.3	671.9	694.2	292	405	21.33
-,-,+	283.7	294.3	574.2	733.9	297	410	21.42
-,-,+	283.7	287.1	574.9	730	289	410	20
-,+,-	281.8	289.3	672.6	687.2	281	400	20.08
-,+,-	283.3	292.3	672.3	781.1	294	400	23
-,-,+	283	294.4	573.6	735.4	297	410	15.93
+,-,-	283	288.8	574.4	717.5	293	395	20
+,+,-	281.8	288.4	672.3	702.1	292	400	20.58
+,-,+	280.7	289.6	574.3	736.9	293	400	20
-,+,-	281.5	289.6	672	725.4	292	400	19.98
-,+,-	281	286.6	672.1	800.9	288	390	20
+,-,-	281.5	286.9	672.1	696.6	291	400	20
-,+,-	280.1	289	672.9	793.1	290	400	20.02
+,-,-	282.2	286.2	574.6	733.7	289	395	20
+,-,-	282.1	286.9	671.7	691	290	395	19.98
+,-,+	279.9	289.2	574.6	810.7	292	390	20.02
+,-,+	280.4	285.9	671.2	805.7	287	380	20
+,-,+	281.9	289.7	672.6	808.4	290	390	19.98
+,-,+	282.6	286.5	669.8	709.4	290	390	20.15
Averages	281.7	289.57	623.2	738.2417	292	400.83	20.2

Table 12: Calculated data

Conversion				Efficiency/Conversion			
Config.	Trial 1	Trial 2	Trial 3	Config.	Trial 1	Trial 2	Trial 3
-,-,-	48.15	60.50	65.63	-,-,-	0.17	0.19	0.10
+,-,-	58.01	64.70	62.49	+,-,-	0.20	0.14	0.22
-,-,-	59.23	60.71	59.83	-,-,-	0.14	0.14	0.20
+,-,-	63.75	73.94	72.54	+,-,-	0.17	0.09	0.10
-,-,+	64.93	63.96	63.00	-,-,+	0.15	0.18	0.16
+,-,+	58.66	62.50	70.97	+,-,+	0.24	0.23	0.14
-,+,-	70.81	68.98	60.16	-,+,-	0.11	0.16	0.30
+,-,+	57.23	34.90	34.05	+,-,+	0.34	0.49	0.42

Table 13: Raw bed temperature data

Temperatures Through Bed										
		Thermocouple Placement (inches bed depth)								
		0	0.1	0.2	0.3	0.4	0.75	1.25	2	2.75
-,-,-		375.25	656.04	658.32	655.12	651.17	641.99	634.38	611.64	436.34
		382.37	649.80	652.75	649.53	646.91	638.46	625.61	609.64	525.92
		373.69	654.07	655.67	653.08	649.13	640.41	632.48	609.37	432.35
Average		377.11	653.30	655.58	652.58	649.07	640.29	630.83	610.22	464.8
+,-,-		390.80	678.46	680.86	676.80	669.85	656.30	645.56	617.41	435.81
		401.49	665.28	662.86	648.42	640.85	627.00	618.42	606.31	520.21
		397.00	692.86	696.64	690.18	681.68	666.30	655.48	625.09	444.34
Average		396.43	678.87	680.12	671.80	664.13	649.87	639.82	616.27	466.79
-,+,-		439.21	677.62	680.84	675.50	668.23	654.24	644.21	615.35	421.08
		459.25	682.22	686.13	679.31	669.14	651.30	638.85	612.48	414.06
		391.69	695.39	698.87	692.96	684.97	670.53	660.20	630.87	460.51
Average		430.05	685.08	688.61	682.59	674.11	658.69	647.75	619.57	431.88
+,+,-		452.21	691.02	694.42	688.66	678.69	661.85	650.29	619.83	429.00
		459.28	698.05	702.43	694.83	684.20	666.32	654.59	622.17	423.43
		471.37	695.21	700.04	691.34	679.06	659.07	645.72	618.09	417.91
Average		460.95	694.76	698.96	691.61	680.65	662.41	650.20	620.03	423.45
-,-,+		355.72	660.10	661.74	659.59	655.20	645.84	636.30	613.84	371.17
		377.67	677.26	679.92	675.86	670.61	659.27	650.47	623.91	456.92
		366.37	663.49	665.79	662.84	659.72	652.27	645.87	622.04	462.29
Average		366.59	666.95	669.15	666.10	661.85	652.46	644.21	619.93	430.13
+,+,+		385.06	693.20	696.71	691.02	683.65	669.32	658.45	629.38	463.74
		391.69	695.39	698.87	692.96	684.97	670.53	660.20	630.87	460.51
		399.17	679.16	676.78	660.75	652.71	637.49	628.20	616.01	537.58
Average		391.97	689.25	690.79	681.58	673.78	659.11	648.95	625.42	487.28
-,+,+		444.78	694.00	697.85	691.85	682.91	667.37	656.72	627.74	452.23
		463.62	683.69	680.31	662.65	653.62	637.36	627.66	614.46	527.78
		455.20	680.38	676.41	660.48	652.41	636.60	626.83	613.60	520.00
Average		454.53	686.02	684.86	671.66	662.98	647.11	637.07	618.60	500.00
+,+,+		480.57	696.15	691.78	671.61	661.59	645.03	635.55	621.42	532.60
		473.84	691.67	686.94	668.51	659.29	643.29	634.06	620.88	535.27
		486.97	717.59	723.57	712.71	698.58	676.67	661.47	630.09	436.21
Average		480.46	701.80	700.76	684.28	673.15	655.00	643.69	624.13	501.36

Autothermal Reforming Procedure

Start-Up Procedure

- ☐ Turn on Gas Chromatograph, ensure 30 psi on N₂ carrier gas and TCD set to low current
- ☐ Turn on on-line gas analyzer (COSA 1600)
- ☐ Turn on sample conditioner (freezer)
- ☐ Turn on Data Acquisition unit using power supply (APC)
- ☐ Turn computers and go to C:\LabView\High Temperature Reformer main 3, or just hit icon on desktop
- ☐ Ensure all vaporizer and superheater switches as well as pump voltages on program are off and start computer program
- ☐ Ensure all wall switches in lab and power supplies in control room are off
- ☐ Fill fuel and water tanks as well as reserve tanks
- ☐ Cap reserve tanks and hook up operating tanks to pumps
- ☐ Turn on scales and weigh fuel and water tanks and mark on each tank its weight
- ☐ Ensure caps to tanks are loose and outlet valves are open
- ☐ Ensure that the exit of the sump pump in the freezer is directed into the condenser
- ☐ Ensure that the drain valve for the sump pump is closed
- ☐ Fill bottom of freezer with approx. 2 inches of ice and fill with water until sump pump is nearly submerged
- ☐ Check operation of the CO/smoke alarms (red light blinking-change battery, green light-OK) there are approx. 20 seconds between blinks
- ☐ Turn on all power strips in lab area and ensure 60 psi regulated on air compressor (air compressor located in bus garage) and connect to air inlet
- ☐ Check volume of liquid in propane tank by weighing tank _____ lbs. and open propane valve (empty weight = 20 lbs.)
- ☐ Turn on exhaust blowers (2) (green lights) and lab evacuation blower

- ☐ Turn on both lab and control room emergency shut-off switches (blue lights)
- ☐ Open valve on CO₂ and regulate pressure to 20 psi
- ☐ Open reformer back pressure valve and the fuel and water flowmeter valves. Leave the hydrogen valve closed
- ☐ Open the valve on the hydrogen tank and regulate to 15 psi.
- ☐ Remove condensate from reformer using center valve below the steel sheet under the reformer and from both condensate lines on exhaust.
- ☐ Direct the vaporized fuel valve below the reformer and just above the steel sheet to drain and place a bucket below for the fuel.
- ☐ Direct the vaporized water valve to the left of the reformer and just above the steel sheet to drain into the bucket below.
- ☐ Ensure power supply knobs for water and fuel to reform pumps turned fully counter-clockwise (off)
- ☐ Turn on multimeters and power supplies (in office)
- ☐ Check operation of high temperature alarm (in office)

In the program

- ☐ Input the desired independent parameters A/F, S/C, Fuel Type, Space Velocity and vaporizer temps
- ☐ Run Program
- ☐ Start airflow at set point flow rate, start air superheaters and Fuel/Air/Water heater as well as Reformer entrance heater. (set all to 200°C)
- ☐ Turn on both fuel vaporizer and superheater controls and start the flow of fuel at the set point flow rate
- ☐ Set hydrogen flowmeter to 15 and observe temperature increase
- ☐ Once fuel past 100°C, start flow of water at set point until water weeping out. Then start water heaters (propane and electric) by turning on the water vaporizer, setting the set point to 400°C igniting the propane burner

To ignite propane burner: Depress and hold down ignite button on computer while igniting propane burner (manual operation) Wait until burner reaches 700°C before releasing computer button

Note: Check ignition by propane thermocouple and visually for blue flame. If ignition trouble, open choke. If hot and burn trouble, close choke.

- ☐ After temperature of the entrance of the catalyst bed increases to over 400°C, use a glove to turn vaporized fuel valve from exhaust to reformer. When temperature begins to increase, turn the vaporized water valve from exhaust to reformer. If temperatures stabilize above 450°C continue, or else turn both fuel and water to exhaust and try again.
- ☐ Turn off hydrogen flow when bed temperature stabilizes
Note: COSA cannot read CO levels greater than 10%

Autothermal Reformer Lab Sampling Data Sheet

Start Date _____ Time _____ Temperature Room _____ C
 Configuration _____ Humidity Room _____ %
 Eq. Rat _____ Inlet Temperature _____ Space Velocity _____ S/C _____

- ☐ Ensure sufficient reactant supply in reserve tanks, ice in the sample conditioner and drain the reformer exhaust
- ☐ Evacuate a sample bag
- ☐ Input new independent parameters
- ☐ Adjust voltages on computer and power supplies to computer suggestions
- ☐ Check air, fuel and water flowrates Air flow _____ SLPM
- ☐ Ensure steady state temperatures for inlet conditions and CO₂ levels in exhaust
- ☐ Open gas sample valve
- ☐ Starting masses: Fuel _____ g Water _____ g
- ☐ Turn lab gas sample pump on
- ☐ Turn on the "Acquire Data" button
- ☐ Take sample at 5 minutes through 10 minute run
- ☐ Temperature flowmeter _____ C, Flow Reading _____, Pressure _____ mmHg
- ☐ Check Analyzer for CO% _____ CO₂% _____ O₂% _____

- ☐ At 10 minute run time **Ending masses Fuel** _____ **g Water** _____ **g**
- ☐ Turn off sample pump
- ☐ Turn off the “Acquire Data” button
- ☐ Turn off gas sampling valve
- ☐ Remove water from top of water separator with rag and unhook
- ☐ Transfer water separator contents to graduated cylinder and analyze
Trapped water _____ **ml Trapped fuel** _____ **ml**
- ☐ Clean both the graduated cylinder and the water separator using DI water
- ☐ Inject sample into GC and find **H₂%** _____

	Low (-)	High (+)
A/F Ratio	0.608	0.672
Space velocity	20,000	25,000
Temperature	300C	400C

A/F Ratio	Inlet Temperature	Space Velocity	Run Order
+	+	+	15,10,24
-	+	+	19,4, 16
+	-	+	9,13,6
-	-	+	2,21,5
+	+	-	1,8,23
-	+	-	3,22,12
+	-	-	14,11,7

-	-	-	18,20,17
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Shutdown

- ☐ Turn off water and fuel to reform power supplies by rotating knobs fully counterclockwise and switch off power supplies
- ☐ Turn off air, water and fuel heaters on computer
- ☐ Monitor reduction in propane burner temperature
- ☐ Hit the emergency shutdown button (push down knob in the office) to allow the flow of CO₂ for approx. 2 min. and turn emergency shut-off back on (pull knob in office)
- ☐ Close valve on hydrogen tank
- ☐ Close valve on propane tank
- ☐ Allow air to cool catalyst bed to ~150°C
 - ☐ Turn off all lab power except for exhaust fans and sump pump
- ☐ Turn off valve on CO₂ bottle
- ☐ Close flowmeter valves
- ☐ Drain freezer using coolant pump
- ☐ Drain COSA condensate and reformer exhaust condensate
- ☐ Turn off exhaust fans and coolant pump
- ☐ Stop program
- ☐ Check volume of liquid in propane tank by weighing tank _____ lbs.

Major Parts of the Lab

Overview

The autothermal reforming rig was designed to study the autothermal and partial oxidation reforming characteristics of various fuels and catalysts. The rig is comprised of five sections: reactant supply, reactant flow control, reactant conditioning, reforming and exhaust, sample conditioning and sample collection (figure 22). The rig uses a LabView based program for system control and data acquisition. Finally, the hardware employs several mechanical and electrical safety measures.

The Building

The Fuel Cell Bus Garage Addition was completed in February 2002 under a Ford Foundation grant to study fuel cells and their associated systems. The circuitry for the addition was designed to house the rig by supplying a dedicated 20-amp breaker to the center-most outlet along the west wall where the rig was located.



Figure 45: Fuel cell bus garage and addition

Reactant Supply Section

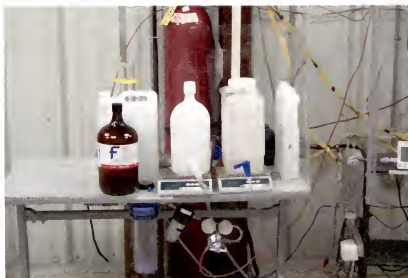


Figure 46:Reactant supply section

Table 14:Reactant supply section parts

Qty.	Parts	Model Number
1	5 L Nalgene fuel tank	N/A
1	7 L Nalgene water tank	N/A
2	5 L Nalgene additional tanks for reactant storage	N/A
3	0 to 5 kg scales	Taylor TE 10
1	Air compressor	Charge Air Pro with 20 gallon tank
1	Carbon Dioxide	20 lb compressed 99%
1	Hydrogen	HY-K size (roughly 240 cubic feet) 99.999%
N/A	Deionized Water	Tap purified by 2 Cole-Parmer Adsorber ION-X and 1 Cole-Parmer Monobed deionizer
N/A	Trimethylpentane2,2,4	Fisher Certified ACS 99.8% and <0.001% Sulfur Compounds

Reactant Flow Section



Figure 47: Reactant flow section

Table 15: Reactant flow section parts

Qty.	Parts	Model Number
1	Parker skinner normally open solenoid valve	71295
1	Wilkerson dessicant dryer	X06
2	Micropump stainless steel gear pumps, 0 - 30 ml/min (fuel) and 5 - 300 ml/min (water)	N/A
3	Flow meters	Omega 3651G-HRV (fuel), 3692C-HRV (water)
1	Mass flow controller	Omega FMA 1900

Reforming and Reactant Conditioning Sections

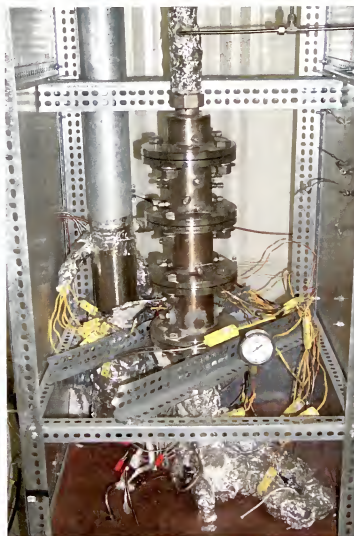


Figure 48: Reforming and reactant conditioning sections

Table 16: Reactant conditioning parts

Qty.	Parts	Model Number
7	Omegalux flexible heavy duty heating tapes	N/A
2	750 watt cartridge heaters 10" long	N/A
1	Parker proportional valve,	BP2EV0005
2	400 watt cartridge heaters 5" long	N/A

Table 17:Reforming section parts

Qty.	Parts	Model Number
8	4", ½" thick stainless steel flanges	N/A
1	3" diameter stainless steel pipe	N/A
1	Synetix catalyst bed, nickel oxide, magnesium oxide, ceramic substrate	Katalco 46-C,
1	3" diameter stainless steel tube	N/A

Exhaust Section



Figure 49:Exhaust section

Table 18:Exhaust section parts

Qty.	Parts	Model Number
2	Tjernlund Side wall vent blower	HUSL-J
1	NUPRO Blow-off valve	RL3
1	RP&C High temperature exhaust ¼" globe valve	N/A
N/A	4" ductwork	N/A
N/A	1" black iron pipe	N/A

Sample Conditioning Section

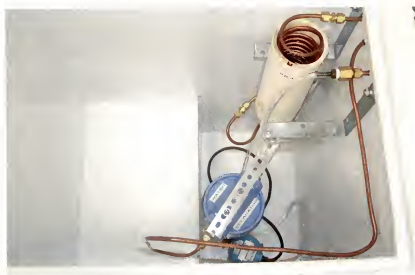


Figure 50: Sample conditioning section

Table 19: Sample conditioning section parts

Qty.	Parts	Model Number
1	Culligan water filter housing	HF-360
1	Frigidaire freezer	MFC05MOBW6
1	Little Giant sump pump	#1 Series

Sample Collection Section



Figure 51: Sample collection section

Table 20: Sample collection section parts

Qty.	Parts	Model Number
1	Cole-Parmer flowmeter	Tube number N044-40
1	Gast vacuum pump	DOA-P104-AA
1	Check valve	Swagelok Series 50
1	Gas Analyzer	COSA 1600 IR

Control System



Figure 52: Control system

Table 21: Control system parts

Qty.	Parts	Model Number
1	Data acquisition program	LabView version 6
1	Laptop computer	Dell Inspiron 3000
2	14 channel Thermocouple boards	Iotech DBK 52
1	4 channel analog output board	Iotech DBK 2
1	24 channel digital output board	Iotech DBK 24
1	Computer interface	Iotech Daq book
2	DC power supply	Samlex PSA-305

Additional Safety Measures

Table 22: Additional safety measure parts

Qty.	Parts	Model Number
1	High temperature alarm	Omega CN355
2	Smoke and CO alarm	Firex

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BIOGRAPHICAL SKETCH

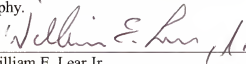
Timothy Curtis Simmons Jr. was born in Gainesville, Florida. He then moved to Carson, California, to complete a portion of his primary education at Chadwick School in Palos Verdes, California. Tim went on to complete his high school education at Kent Denver School in Denver, Colorado. He went on to complete a four-year bachelor's degree at the University of California, San Diego, in 1996 as well as studying briefly at the University of California, Los Angeles, and the Pasadena Art Center College of Design. Following the completion of the bachelor's degree, he went to Flint, Michigan, to complete a master's degree in mechanical engineering with an emphasis in powertrain design at Kettering University. While there, Tim worked to help garner funding and acquire equipment to start a Fuel Cell Lab. Also while a student at Kettering, he studied briefly at Texas A & M University in College Station, Texas, and at the Center for the Creative Studies in Detroit, Michigan. Also during this time, Tim proposed and was awarded a patent for a fuel cell design. Tim began studies towards his doctoral degree at the University of Florida in 1998 under the direction of Dr. Vernon Roan. The area of his research was energy conversion with an emphasis in fuel processing for fuel cell vehicles. At the University of Florida, Tim worked as an instructor in the Instrumentation and Measurement Laboratory, as a teaching assistant and as a researcher in the Fuel Cell Research and Training Laboratory. Tim has used his research at the University of Florida to publish in several technical journals and conferences.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Vernon P. Roan, Chairman
Professor of Mechanical and Aerospace
Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



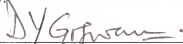
William E. Lear Jr.
Associate Professor of Mechanical and
Aerospace Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



David W. Hahn
Assistant Professor of Mechanical and
Aerospace Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



D. Yogi Goswami
Professor of Mechanical and Aerospace
Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Jean M. Andino
Associate Professor of Environmental
Engineering Sciences

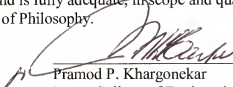
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Paul Mason
Assistant Professor of Mechanical and
Aerospace Engineering

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August, 2003



Pramod P. Khargonekar
Dean, College of Engineering

Winfred M. Phillips
Dean, Graduate School